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TABLE OF CONTENTS

Vol. 27 July 1, 1944 No. 7

THE JOURNAL

Investigation of Reactions of Simple Magnesia Spinels with Alkaline Earth Orthosilicates in Solid State 197–202

By V. D. Fréchette and A. I. Andrews

Study of Factors Involved in Glaze-Slip Control, I–IV

I, Glaze-Slip Specifications 202–207

By C. G. Harman and C. F. Schaefer

II, Correlation of Glaze Thickness with Air Permeability 207–209

By C. G. Harman and M. K. Blanchard

III, Additional Glazes and Improved Technique and Apparatus 209–214

By C. G. Harman and H. C. Johnson

IV, Practical Uses for Coherence Value and Receptivity Measurements 214–220

By C. G. Harman and H. C. Johnson

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INVESTIGATION OF REACTIONS OF SIMPLE MAGNESIA SPINELS WITH ALKALINE EARTH ORTHOSILICATES IN THE SOLID STATE*

By V. D. Fréchette and A. I. Andrews

Abstract

The spinels $MgO \cdot Al_2O_3$, $MgO \cdot Cr_2O_3$, and $MgO \cdot Fe_2O_3$ and the orthosilicates $2MgO \cdot SiO_2$, $2CaO \cdot SiO_2$, $2SrO \cdot SiO_2$, and $2BaO \cdot SiO_2$ were synthesized by solid-state reaction of the component oxides or compounds yielding the oxides on ignition. Each of the spinels was tested at various temperatures with each orthosilicate in turn by placing a pellet of each in contact and also by intimately mixing the two. Petrographic microscopy and X-ray diffraction were employed in the identification of reaction products.

I. Introduction

With the many recent developments in the technology and manufacture of chrome-magnesite refractories, considerable attention has been attracted to the fundamental nature of these materials and their reactions with other materials. The appreciation of the limited knowledge of this subject and the desirability for more definite information led to the present investigation, which deals primarily with the solid-state reactions of magnesia spinels and the alkaline earth orthosilicates.

II. Review of the Literature

It is only within comparatively recent years that reactions between solids in the absence of a liquid phase have been recognized. These solid-state reactions, however, are now well known and are receiving the attention of many investigators. The subject of solid-state reactions has been treated recently in detail by Jost[1] and Hedvall.[2] Barrer[3] has given detailed consideration to the process of diffusion into and through solids, and Taylor[4] has reviewed the subject briefly with special reference to its ceramic implications.

A few of the salient principles governing solid-state reactions of the type usually encountered in ceramics may be summarized as follows:

(1) The transfer of material by diffusion is one of the controlling factors in the progress of many solid-state reactions. Jost† points out that it is not simply a case of infiltration of solute into solvent, as with fluid solutions, but it is generally a process of exchange in which material passes into body 2 from body 1 while at the same time an equivalent amount of material passes from body 2 into body 1.

Fick's first law of diffusion is shown in equation (1).

$$s_{i_2} = -q \cdot D_i \cdot dc_i/dx \qquad (1)$$

This law states that the amount of component i passing through cross-section q, perpendicular to the direction of decreasing concentration (x direction) in unit time is proportional to the concentration drop; the proportionality factor, D_i, is defined as the diffusion coefficient. Fick's second law, given in equation (2), expresses the change of concentration with time.

$$\frac{\partial c_i}{\partial t} = D_i\left(\frac{\partial^2 c_i}{\partial X^2} + \frac{\partial^2 c_i}{\partial Y^2} + \frac{\partial^2 c_i}{\partial Z^2}\right) \qquad (2)$$

The second law is based on the assumption that the diffusion coefficient is independent of concentration; this is rarely true of solids so that its use is greatly restricted although it remains important as an approximation for use in practical calculations.

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* Presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, Inc., Pittsburgh, Pa., April 21, 1943 (Refractories Division). Received March 7, 1944.

Based on a thesis submitted by the senior author in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Engineering, Department of Ceramic Engineering, University of Illinois, Urbana, Ill., June, 1942.

[1] Wilhelm Jost, Diffusion und chemische Reaktion in festen Stoffen. Theodor Steinkopff, Dresden and Leipzig, 1937; *Ceram. Abs.*, **17** [8] 292 (1938).

[2] J. A. Hedvall, Reaktionsfähigkeit fester Stoffe. Johann Ambrosius Barth, Leipzig, 1938. 243 pp.; *Ceram. Abs.*, **17** [4] 164 (1938).

[3] R. M. Barrer, Diffusion in and Through Solids. Cambridge Univ. Press, Cambridge, 1941. 464 + xiii pp.; *Ceram. Abs.*, **21** [8] 179 (1942).

[4] (*a*) N. W. Taylor, "Reactions in Solids in Absence of Liquid Phase," *Jour. Amer. Ceram. Soc.*, **17** [6] 155–63 (1934).

(*b*) G. R. Pole and N. W. Taylor, "Kinetics of Solid-Phase Reactions of Certain Carbonates with Mullite, Silica, and Alumina," *ibid.*, **18** [11] 325–37 (1935).

† Wilhelm Jost, see p. 9 of footnote 1.

(2) The reaction temperature of a mixture (considered as the point at which the course of the heating curve shows an accelerated rise as the result of the heat of reaction) is the same as the conversion temperature of that component of the mixture which has the lowest conversion temperature.* (The conversion temperature of a material is the lowest temperature at which recrystallization will occur.)

(3) The first product to appear in a solid-state reaction of two reactants with which more than one compound is possible apparently does not depend on the relative amounts of the reactants.† In reactions between CaO and SiO_2 in the absence of liquid, for example, $2CaO \cdot SiO_2$ is the primary reaction product[5] although this compound may react later with excess CaO to form $3CaO \cdot SiO_2$ or with excess SiO_2 to form $CaO \cdot SiO_2$. Jander[6] states that orthosilicates are the primary products in all binary solid-state reactions between silica and the alkaline earth oxides.

(4) In diffusion through solids, not uncharged particles but ions migrate. Wagner[7] has shown evidence that it is generally the metal that migrates through the layer of reaction products in the form of ions plus electrons.

(5) The newly formed crystal phase appearing as a product of solid-state reaction shows a defect lattice[8] and, as a result, a high reactivity.[9] The lattice defects decrease and the reactivity diminishes through further heat-treatment. An associated phenomenon is termed by Hüttig[10] the "memory" of materials. He showed, as an example of this, that whereas the gamma-alumina prepared by careful dehydration of aluminum hydroxide gel rehydrated to an amorphous gel, the same oxide prepared from crystalline bayerite rehydrated by corresponding treatment to crystalline bayerite.[11]

(6) The influence of the fineness of the reactants is well known. Chesters and Parmelee[12] studied reaction rates by means of expansion measurements; they found that a mixture of magnesia and alumina containing only 0.15 mm. material reacted to form spinel only half as fast as 0.06 mm. material.

(1) Synthesis of Spinels and Orthosilicates

Because the spinels and orthosilicates are stable at all temperatures up to their melting points, it is possible to prepare them by crystallization from melts of appropriate compositions.[13] The preparation of the pure compounds by this means, however, is extremely difficult because of their high melting points.

Parmelee, Badger, and Ballam[14] have discussed the various methods of spinel synthesis. They found the "wet" method of Berzelius, Sander, and others to be impractical because of the difficulty experienced in washing and filtering the gelatincus precipitates which were formed. They also discarded the method used by Daubree, Deville, Caron, and others, involving the vaporization of metallic fluorides in the presence of lime or boric oxide. A modification of the method of Ebelmen[15] was finally chosen. This method consisted of heating a mixture of the oxides together with boric oxide at 900° to 1300°C., depending on the type of spinel, for 24 to 48 hours. Excess of the basic oxide was used in the difficult cases; this was removed after firing by leaching with acid. Hugill[16] also reported success in synthesizing spinels by this means.

Noda and Hasegawa[17] investigated the effect of fluorides and chlorides on spinel synthesis. They listed the salts in the following order of decreasing effectiveness: LiX, NaX, KX; MgX_2, CaX_2, SrX_2, BaX_2; and AF, ACl, BF_2, BCl_2, wherein A designates an alkali metal, B an alkaline earth metal, and X a fluoride or chloride. Magnesioferrite ($MgO \cdot Fe_2O_3$) was synthesized by Nacken and Grunewald[18] by heating the oxides in the presence of HCl gas at 900° to 950°C., using a platinum catalyst. Dilaktorskil[19] described synthesis of a number of spinels by this method. Bénard and Chaudron[20] prepared $MgO \cdot Fe_2O_3$ and other ferrites by the substitution of a divalent oxide for the FeO in magnetite. They found that only the spinel-forming protoxides would react in this way. Seil[21]

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* Wilhelm Jost, see p. 211 of footnote 1.

† J. A. Hedvall, see p. 124 of footnote 2.

[5] W. Jander and E. Hoffman, "Reactions in Solid State at High Temperatures: XI, Reaction Between CaO and SiO_2," *Z. Anorg. Allgem. Chem.*, **218**, 211–23 (1934).

[6] W. Jander, "Reactions in Solid State: II, Course of Reactions in Solid State," *Angew. Chem.*, **49**, 879–82 (1936); *Ceram. Abs.*, **16** [10] 313 (1937).

[7] C. Wagner, "Theory of Tarnishing Process," *Z. Physik. Chem.*, **B21**, 25–41 (1933).

[8] G. Tammann, "Transformations in Crystals with Lattice Defects," *Z. Anorg. Allgem. Chem.*, **233**, 286–94 (1937).

[9] W. Jander and H. Hermann, "Reactions in Solid State at High Temperatures: XXIII, Theory of Active Form Which Appears at Beginning of Reaction in Solid State," *ibid.*, **241**, 225–32 (1939).

[10] G. F. Hüttig and E. Frantz, "'Memory' of Solid Materials," *ibid.*, **231**, 104–10 (1937).

[11] G. F. Hüttig and F. Kölbl, "Active Oxides: LXVII, Aluminum Oxides and Their Addition Compounds with Water," *ibid.*, **214**, 289–306 (1933).

[12] J. H. Chesters and C. W. Parmelee, "Measurement of Reaction Rates at High Temperatures," *Jour. Amer. Ceram. Soc.*, **17** [3] 50–57 (1934).

[13] A. Bazilevich, "Synthesis of Spinels," *Mineral Suir'e*, **9** [9] 25–30 (1934); *Ceram. Abs.* **14** [11] 282 (1935).

[14] C. W. Parmelee, A. E. Badger, and George Ballam, "Study of Group of Typical Spinels," *Univ. of Ill. Eng. Expt. Station Bull.*, No. 248, 56 pp. (1932); *Ceram. Abs.*, **13** [10] 265 (1934).

[15] M. Ebelmen, *Ann. chim. phys.*, **3**, 22, 211 (1848); **3**, 33, 34 (1851).

[16] W. Hugill, "Preparation and Properties of Some Synthetic Spinels," *Iron & Steel Inst. (London), Special Rept.*, No. 26, pp. 201–204 (1939); *Ceram. Abs.*, **19** [5] 116 (1940).

[17] Tokiti Noda and Masotosi Hasegawa, "Effect of Addition of Salt Vapor on Synthesis and Crystal Growth of Spinel," *Jour. Soc. Chem. Ind. Japan*, **43** [3] 169–72 (1940); *Ceram. Abs.*, **20** [3] 76 (1941).

[18] R. Nacken and M. E. Grunewald, "Chemical Combinations of Lime and Magnesia with Ferric Oxide," *Zement*, **15**, 561–62, 576–78, 589–91, 614–16 (1926); *Ceram. Abs.*, **7** [1] 54–55 (1928).

[19] N. L. Dilaktorskil, "Synthesis of Some Minerals of the Spinel Group," *Zapiski Vserossiĭskogo Mineral. Obshchestva*, **68** [1] 18–26 (1939); *Ceram. Abs.*, **19** [11] 270 (1940).

[20] J. Bénard and Georges Chaudron, "Preparation of Ferrites by Substitution for Ferrous Ions in Magnetite," *Compt. Rend. Acad. Sci., U.R.S.S.*, **204**, 766–68 (1937).

[21] G. E. Seil and Staff, "Orthosilicates of the Alkaline Earths with Special Reference to Their Uses in the Refractory Field," *Jour. Amer. Ceram. Soc.*, **24** [1] 1–22 (1941).

found that, in the formation of forsterite from the oxides at 2600° to 3040°F., the reaction was retarded by the presence of small amounts of P_2O_5, B_2O_3, or Cr_2O_3. He was able to synthesize all of the orthosilicates in the absence of mineralizers.

Spinels and orthosilicates have been synthesized by many investigators by solid-state reaction of the oxides or compounds yielding the oxides on iguition without the use of mineralizers. Indeed, a large part of the solid-state reaction theory has been based on observations made in the study of the synthesis of these two families of minerals.

(2) Description of Minerals

The spinels are a family of minerals of the general chemical formula $RO \cdot R_2O_3$, in which the divalent metal may be one or more of Mg, Fe, Cu, Zn, Ni, Co, or Mn and the trivalent metal may be one or more of Al, Fe, Mn, Ga, or Cr; they crystallize in the isometric system commonly as octahedra or dodecahedra. Simple spinels (consisting of a single divalent and a single trivalent metal) rarely appear in nature, but they may be formed synthetically. Parmelee and Badger and their co-workers[22] have published an extensive reference list of the findings of early investigators; they prepared the aluminates, ferrites, and chromites of Zn, Mg, Fe, and Mn and measured their scratch hardnesses, densities, lattice dimensions, heat capacities, and thermal expansions.

Table I is a compilation of some of the properties of the simple spinels used in this investigation.

According to Winchell,[23] forsterite ($2MgO \cdot SiO_2$) occurs in short prismatic colorless crystals with distinct 001 and 010 cleavages. Its specific gravity is 3.216 and it melts at 1910°C.

Dicalcium silicate ($2CaO \cdot SiO_2$) appears to be the only one of the orthosilicates to show polymorphism. Lea and Desch[24] describe these modifications in detail. The alpha modification is stable from 1420°C. to its melting point at 2130°C., occurring in irregular grains intricately interwoven and twinned and occasionally showing prismatic development. Its specific gravity is 3.27. Beta-dicalcium silicate is stable in the range 675° to 1420°C.; it changes reversibly at 675°C. from the beta to the gamma form. When formed from the alpha modification, it is pseudomorphic with it; otherwise it appears as irregularly rounded grains without the intricate twinning that characterizes the high-temperature form. The specific gravity is 3.28. Gamma-$2CaO \cdot SiO_2$ is stable below 675°C.; from the beta modification, it is obtained as a fine powder. It is prismatic in development with perfect cleavage along the prism axis and shows nearly parallel extinction. The specific gravity of 2.974 is decidedly lower than the other forms; this results in an expansion of nearly 10% on inversion of dicalcium silicate to the gamma form. Small amounts of B_2O_3 or P_2O_5 tend to stabilize both of the high-temperature forms, but more especially the alpha modification, against inversion on cooling.

Less is known about the properties of the orthosilicates of strontium and barium. The fusion points

TABLE I

PROPERTIES OF SOME SIMPLE SYNTHETIC SPINELS*

	$MgO \cdot Al_2O_3$	$MgO \cdot Cr_2O_3$	$MgO \cdot Fe_2O_3$
Moh's scale hardness	7.5	6.5	5.5
Pycnometer density	3.53	4.41	4.61
Lattice dimensions (a.u.)	8.064†	8.305	8.366
Computed density	3.548	4.429	4.506
Heat capacity (50°–1025°C.)	1.19(joules/gm./°C.)	0.92	0.86
Linear thermal (expansion) (25°–900°C.)	81×10^{-7}	93×10^{-7}	129×10^{-7}
Refractive index	1.72_D*	2.08_D§	2.34_{Li}**
Melting point	2135°C.‡	2250°C.‖	††

* Data are taken from Parmelee, Badger, and Ballam (footnote 14), except where otherwise noted.

† See footnote 22 (*c*).

‡ G. A. Rankin and H. E. Merwin, "Ternary System $MgO–Al_2O_3–SiO_2$," *Amer. Jour. Sci.*, [4th series], **45**, 301–25 (1918).

§ See footnote 23.

‖ K. J. A. Bonthron and Robert Durrer, "Studies for Determination of Melting Diagrams of System $Al_2O_3–Cr_2O_3–MgO$," *Z. Anorg. Allgem. Chem.*, **198**, 141–56 (1931).

** See footnote 19.

†† (*a*) H. G. Fisk and W. J. McCaughey, "Equilibrium Studies in Systems Containing Magnesium Oxide, Iron Oxide, and Magnesium Aluminate," *Ohio State Eng. Expt. Station Bull.*, No. 70, pp. 1–44 (1932); *Ceram. Abs.*, **12** [3] 128 (1933).

(*b*) M. E. Grunewald, Systems $CaO–Fe_2O_3$ and $MgO–Fe_2O_3$. Inaugural Dissertation, Frankfurt a. M. (1926).

Fisk and McCaughey state that according to Grunewald "an alteration" took place along the octahedral edges of $MgO \cdot Fe_2O_3$ above 1350°C. Grunewald was unable to say whether this was the partial melting or other transformation. At 1450°C., the change was quite pronounced, but up to 1500°C., no complete melting had taken place.

TABLE II

OPTICAL PROPERTIES OF ALKALINE EARTH ORTHOSILICATES

	Indices of refraction			Birefringence
	N_p	N_m	N_g	$N_g–N_p$
$2MgO \cdot SiO_2$	1.636	1.651	1.669	0.033
α-$2CaO \cdot SiO_2$	1.715	1.720	1.737	.022
β-$2CaO \cdot SiO_2$	1.717		1.735	.018
γ-$2CaO \cdot SiO_2$	1.642	1.645	1.654	.012
$2SrO \cdot SiO_2$	1.727	1.732	1.756	.029
$2BaO \cdot SiO_2$	1.810		1.830	.020

[22] (*a*) G. L. Clark, Abde Ally, and A. E. Badger, "Lattice Dimensions of Spinels," *Amer. Jour. Sci.*, **22** [133] 539–46 (1931); *Ceram. Abs.*, **12** [1] 20 (1933).

(*b*) C. W. Parmelee and Abde Ally, "Some Properties of Chrome Spinel," *Jour. Amer. Ceram. Soc.*, **15** [4] 213–25 (1932).

(*c*) G. L. Clark, E. E. Howe, and A. E. Badger, "Lattice Dimensions of Solid Solutions in the System $MgO–Al_2O_3$," *ibid.*, **17** [1] 7–8 (1934).

See also footnote 15.

[23] A. N. Winchell, Microscopic Characters of Artificial Inorganic Solid Substances or Artificial Minerals. 2d ed. John Wiley and Sons, New York, 1931. xvii + 403 pp.; *Ceram. Abs.*, **11** [8] 468 (1932).

[24] F. M. Lea and C. H. Desch, Chemistry of Portland Cement and Concrete. Edward Arnold & Co., London, 1935. xii + 429 pp.; *Ceram. Abs.*, **15** [9] 267 (1936).

TABLE III

SYNTHESIS OF COMPOUNDS

Compound	Mineral name	Theoretical compositions (%)		Batch materials	Temp. of synthesis (°C.)
$MgO \cdot Al_2O_3$	Spinel	28.4	MgO	Al_2O_3, MgO, $Mg(OH)_2$	1350
		71.6	Al_2O_3		
$MgO \cdot Cr_2O_3$	Picrochromite	21.0	MgO	Cr_2O_3, MgO, $Mg(OH)_2$	1350
		79.0	Cr_2O_3		
$MgO \cdot Fe_2O_3$	Magnesioferrite	20.1	MgO	Fe_2O_3, MgO, $Mg(OH)_2$	1250
		79.9	Fe_2O_3		
$2MgO \cdot SiO_2$	Forsterite	57.3	MgO	MgO, $Mg(OH)_2$, $SiO_2 \cdot xH_2O$	1400
		42.7	SiO_2		
$2CaO \cdot SiO_2$	Larnite (α-) / Shannonite (β-)	65.1	CaO	CaO, $SiO_2 \cdot xH_2O$	1350
		34.9	SiO_2		
$2SrO \cdot SiO_2$	Strontium orthosilicate	77.5	SrO	$Sr(C_2H_3O_2)_2 \cdot {}^1/_2H_2O$	1350
		22.5	SiO_2	$SiO_2 \cdot xH_2O$	
$2BaO \cdot SiO_2$	Barium orthosilicate	83.6	BaO	$BaCO_3$, $SiO_2 \cdot xH_2O$	1350
		16.4	SiO_2		

apparently approximate that of platinum (1773°C.) or higher. Barium orthosilicate is described by Winchell as granular without cleavage or twinning, whereas strontium orthosilicate is commonly twinned on 100; both are colorless.

Seil compiled the literature on the orthosilicates of the alkaline earths[25] and summarized[21] the optical properties of the alkaline earth orthosilicates as listed in Table II.

(3) Orthosilicate-Spinel Reactions

No trace was found in the literature of work having been done in this field.

III. Experimental

(1) Synthesis of Compounds

Spinels and orthosilicates were synthesized from reagent-quality chemicals by reaction at elevated temperatures in the solid state. The batches, amounting in each case to 20 gm. on the ignition loss-free basis, were calculated to yield oxides in the molecular ratios of the compounds sought as indicated in Table III.

Intimate mixing was accomplished by grinding the materials together in an agate mortar. The mixture was fired in a platinum-wound tube furnace under automatic potentiometer control, the temperature being checked periodically by means of a second thermocouple and a precision portable potentiometer (this equipment was used also in the reaction tests).

The powder sample, contained in a platinum crucible, was lowered into the hot furnace and withdrawn at the end of an hour. After thorough regrinding, it was returned to the furnace, and the process was repeated until microscopic examination showed complete homogeneity of the product. In most cases, six such one-hour firings were found sufficient to effect complete conversion although considerably longer time was required in the case of forsterite. The compounds were stored over sulfuric acid and checked against published data by X-ray diffraction measurements and petrographic examination.

(2) Mixture Reaction Tests

These tests were designed to determine whether or not reactions occurred and to give information as to the identity of the products of the reactions. A spinel was mixed intimately with an orthosilicate in each test by grinding weighed quantities of the two together in an agate mortar. Two mixes were prepared, one in which the proportions were 1 to 1 by weight and the other 2 to 1, molecularly, so that the molecular ratio of the RO groups in the spinel and orthosilicate was 1 to 1. The mixture was fired for one hour at 1400°C. in the tests with $MgO \cdot Al_2O_3$ and $MgO \cdot Cr_2O_3$ and at 1300°C. in tests with $MgO \cdot Fe_2O_3$; they were then cooled and ground fine. This procedure was repeated until six firings had been made, after which the specimen was examined by X-ray diffraction and petrographic methods.

(3) Diffusion Reaction Tests

In an effort to gauge the relative effects of diffusion in the reactions, a small pellet of each orthosilicate was placed on a pellet of each spinel and fired in platinum for twenty-four hours. The pair was then removed and mounted in Canada balsam for grinding and polishing. The specimens were examined with the binocular microscope, using oblique illumination, and with the petrographic microscope, using vertical illumination.

IV. Results and Discussion

(1) Reaction Tests with $MgO \cdot Al_2O_3$

(*A*) *$2MgO \cdot SiO_2$:* No evidence of chemical interaction between $2MgO \cdot SiO_2$ and $MgO \cdot Al_2O_3$ was observed.

(*B*) *$2CaO \cdot SiO_2$:* At 1400°C., there was no evidence of reaction in the diffusion test specimen and the dicalcium silicate dusted and fell away as seen in Fig. 1. In the fired mixture, the gamma modification of $2CaO \cdot SiO_2$ was not observed, and the spinel index was found to have decreased slightly. X-ray examination did not show any new compound. Reaction was vio-

[25] G. E. Seil and Staff, "Bibliography on Orthosilicates of Alkaline Earths with Special Reference to Their Use in the Refractory Field," complete bibliography in *Ceram. Abs.*, **19** [11] 273–93 (1940).

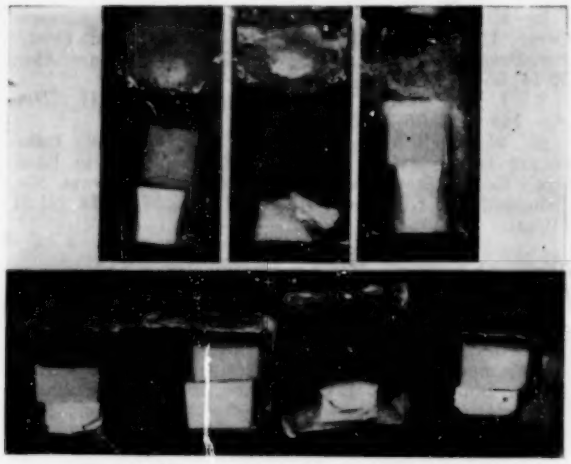

FIG. 1.—Diffusion test specimens with $MgO \cdot Al_2O_3$; *upper row*, $2BaO \cdot SiO_2$, $2SrO \cdot SiO_2$, $2MgO \cdot SiO_2$, fired at 1500°C.; *lower row*, $2BaO \cdot SiO_2$, $2SrO \cdot SiO_2$, $2CaO \cdot SiO_2$, $2MgO \cdot SiO_2$, fired at 1400°C. (The upper briquette is orthosilicate; the lower is $MgO \cdot Al_2O_3$.)

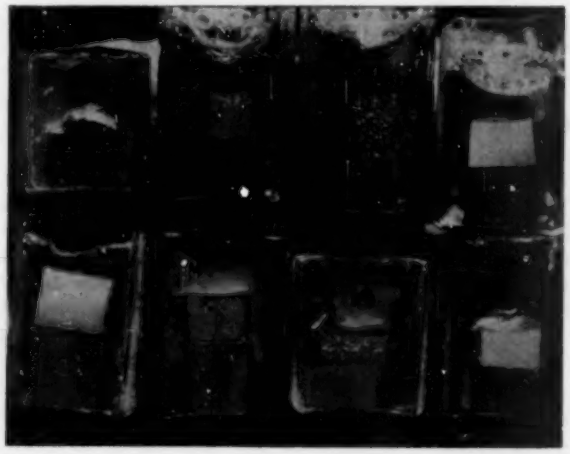

FIG. 2.—Diffusion test specimens with $MgO \cdot Cr_2O_3$; *upper row*, $2BaO \cdot SiO_2$, $2SrO \cdot SiO_2$, $2CaO \cdot SiO_2$, $2MgO \cdot SiO_2$, fired at 1500°C.; *lower row*, $2BaO \cdot SiO_2$, $2SrO \cdot SiO_2$, $2CaO \cdot SiO_2$, and $2MgO \cdot SiO_2$, fired at 1400°C. (The upper briquette is orthosilicate; the lower, $MgO \cdot Cr_2O_3$.)

FIG. 3.—Diffusion test specimens with $MgO \cdot Fe_2O_3$; $2BaO \cdot SiO_2$, $2SrO \cdot SiO_2$, $2CaO \cdot SiO_2$, $2MgO \cdot SiO_2$, fired at 1300°C. (The upper briquette is orthosilicate; the lower, $MgO \cdot Fe_2O_3$.)

lent at 1500°C., causing complete disappearance of the orthosilicate crystalline phase and yielding a glass of index about 1.64.

(*C*) *$2SrO \cdot SiO_2$:* No evidence of reaction was noted in the diffusion test specimen fired at 1400°C., shown in Fig. 1; the separation of the briquettes occurred after removal from the furnace, and little or no adherence developed between them. The mixture had reacted, however, as evidenced by the presence of a small amount of a new anisotropic phase whose optic character was that of $SrO \cdot Al_2O_3$. The absence of any other observable reaction product leads to the supposition that the reaction proceeded by the replacement of SrO by MgO in the orthosilicate. At 1500°C., the test briquettes slumped considerably, as may be seen in Fig. 1.

(*D*) *$2BaO \cdot SiO_2$:* Virtually all of the barium orthosilicate had disappeared from the mixture fired at 1400°C., leaving residual spinel grains inclosed in an unidentified, clear monotropic medium whose index of refraction was 1.695. At 1400°C., there was no evidence of reaction in the diffusion specimens, however, and very little attack was evident at 1500°C., where only a thin zone of penetration of the spinel by the orthosilicate could be observed.

(2) Reaction Tests with $MgO \cdot Cr_2O_3$

(*A*) *$2MgO \cdot SiO_2$:* There was no chemical interaction between $2MgO \cdot SiO_2$ and $MgO \cdot Cr_2O_3$ at 1400° or 1500° C. The diffusion test specimens are shown in Fig. 2.

(*B*) *$2CaO \cdot SiO_2$:* A slight lowering of the refractive index of the $MgO \cdot Cr_2O_3$ was observed in the powder mixture fired at 1400°C., and the gamma (low-temperature) form of $2CaO \cdot SiO_2$ was absent. The diffusion test specimen fired at 1400°C. (Fig. 2) showed a marked blue-green coloration in the $2CaO \cdot SiO_2$ briquette in which the depth of color decreased in intensity with increasing distance from the interface but was uniform from side to side. The spinel was paler in color near the interface, and the gradation of color showed discontinuities appearing as bands in both briquettes. The interaction presumably consisted of a migration of chromium from the spinel, counterbalanced by a migration of silicon from the orthosilicate.

(*C*) *$2SrO \cdot SiO_2$:* Petrographic study of the mixture fired at 1400°C. revealed a change only in the orthosilicate, which appeared pleochroic in blue-colorless. The diffusion specimen at 1400°C. was similar in appearance to that of $MgO \cdot Cr_2O_3$ with $2CaO \cdot SiO_2$; at 1500°C., however, there was an outward flowage at the interface and the color changes were accentuated.

(*D*) *$2BaO \cdot SiO_2$:* In the powder mixture fired at 1400°C., forsterite was identified and the $2BaO \cdot SiO_2$ was strongly colored yellow under the microscope. The appearance of the diffusion briquettes at this temperature (Fig. 2) was analogous to those observed with $2CaO \cdot SiO_2$ and $2SrO \cdot SiO_2$, but the color changes were developed to a much lesser extent. The diffusion specimen fired at 1500°C. indicated a severe reaction. The $2BaO \cdot SiO_2$ disappeared completely, evidently by a fluxing action between the $2BaO \cdot SiO_2$ and the

products of reaction that then flowed down into the spinel briquette, which itself was deformed scarcely at all.

(3) Reaction Tests with $MgO \cdot Fe_2O_3$

Reaction tests with $MgO \cdot Fe_2O_3$ were run only at 1300°C. because of the anomalous "alteration" of $MgO \cdot Fe_2O_3$ at 1350°C. and because of its dissociation in air at higher temperatures. No evidence of reaction of $MgO \cdot Fe_2O_3$ with any of the orthosilicates used was noted at 1300°C., either in the mixtures or in the diffusion specimens shown in Fig. 3.

V. Summary

The results of this investigation show definite tendencies, but because surface characteristics and subsequent histories of minerals are believed to have an appreciable effect on their solid-state reactions, as pointed out by Tammann and others, further investigation should be conducted on these minerals.

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Acknowledgment

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New York State College of Ceramics
Alfred, New York

STUDY OF FACTORS INVOLVED IN GLAZE-SLIP CONTROL, I–IV*
I, GLAZE-SLIP SPECIFICATIONS

By C. G. Harman and C. F. Schaefer

Abstract

Experiments were conducted to find a simple, adequate means of specifying glaze consistency. Tests showed that the amount of slip clinging to a glass plate after it is withdrawn from a reservoir of slip (known as its coherence value) was directly influenced by such factors as amount of water, clay content, and age. These factors are commonly thought of as governing the working quality of the slip. Surface tension has little apparent relation to the working qualities of the slip. Examination of the fired glazes revealed that a distinct coherence value separated good glazes from poor types. A total of 110 pieces was fired; of these samples, fifty-two were glazed with slips having coherence values above 0.04 gm. per sq. cm. Only three of the fifty-two samples were satisfactory; the remaining fifty-eight were coated with slips with a coherence value of less than 0.04 gm. per sq. cm. Only nine of these were defective in any respect and most of them were in the region of 0.04 gm. per sq. cm. coherence value.

I. Introduction

The general flow curve of slips is shown in Fig. 1. This curve may be divided into six segments, according to the character of flow that occurs. Blair[1] has shown that a small but definite stress, called stage (1) and represented by (*a*) in Fig. 1, is required before any flow at all occurs. Upon application of stresses greater than (*a*), stage (2) is reached where the flow curve is rectilinear and the slip moves through the tube as a solid "plug" with no shearing of the slip and no velocity gradient. This plug is regarded as flowing through a water envelope adhering to the walls of the tube. The intercept (*a*) is the shearing strength of the water envelope or film.† This type of flow continues as the pres-

* Part I of this series was presented at the Forty-Second Annual Meeting, The American Ceramic Society, Toronto, Canada, April 9, 1940 (White Wares Division). Received April 9, 1940 (returned to author for completion of work). Parts II, III, and IV were presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 20, 1943. Complete series received October 4, 1943; revised copy received March 31, 1944.

All of the work was conducted under the direction of C. G. Harman, Department of Ceramic Engineering, University of Illinois, Urbana. Part I was prepared by the junior author, C. F. Schaefer, from a thesis to satisfy, in part, the requirements for the degree of Bachelor of Science. Part II was done under an Edward Orton, Jr., Ceramic Foundation Fellowship by the junior author, M. K. Blanchard, during the 1939–1940 term. Parts III and IV were completed by H. C. Johnson during the 1940–1941 and 1941–1942 terms, also under an Edward Orton, Jr., Ceramic Foundation Fellowship.

[1] G. W. S. Blair, "Measurements of Plasticity of Clays," *Jour. Phys. Chem.*, **35** [1] 374–82 (1931); *Ceram. Abs.*, **10** [3] 224 (1931).

† Stress (*a*) is very small and the rate of flow in stage (2) is much less than that of free water or slip under corre-

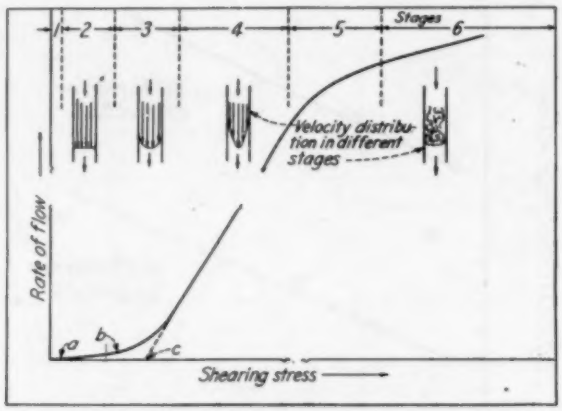

FIG. 1.—Typical flow-stress curve of slips.

sure or stress is increased until the shearing stress of the slip near the walls of the tube has been exceeded. The flow curve becomes curvilinear at this point, and stage (3) begins. Further increases of pressure or shearing stress cause greater portions of slip to move by streamline flow until the core, or plug, of slip moving without shear disappears entirely. When this point has been reached, there is a continuous velocity gradient in the slip from the walls of the tube to the center. In this stage, known as stage (4), the flow is again rectilinear and the slip is moving entirely by streamline flow. When the straight line of stage (4) is extrapolated to the pressure or shearing-stress axis, the intercept is Bingham's yield value. The slope of this part of the curve is the mobility of the slip. Stage (5) is a transition between streamline and turbulent flow, which occurs at still higher rates of flow.

All the types or stages of flow, represented in Fig. 1, can be made to operate simultaneously during the withdrawal of a plate or rod from slip and ordinarily do occur during the glazing operation. Turbulent flow is not so important in ceramic glazing operations; in cases where it is obtained, such fast-moving slip does not remain on the surface to form part of the glaze coating. The static coating and the more slowly moving layer of glaze, together with the intermediate transition layer, are of direct interest in glazing and all will be represented by the layer of glaze adhering to a withdrawn surface.

Some work has been done with viscous liquids by the plate-and-rod withdrawal method. Stott, Turner, and Sloman[2] and Goucher and Ward[3] have demonstrated that the method can be used for the determination of the viscosity of liquids. These tests showed that the thickness of the film adhering to a solid object after withdrawal from a liquid depends on speed of withdrawal and on the viscosity, surface tension, and density of the liquid. Mathematical investigations by Jefferys[4] and subsequent experimental work by Satterly and his associates[5] have shown that the profile of the film is parabolic although the surface appears plane to the unaided eye. These facts demonstrate that the mechanism of flow near a surface being withdrawn from a liquid is the same as that near the surface of a tube through which a liquid may be made to flow. The rate of shear of the liquid varies in both cases from a minimum value near the solid surface to a maximum at some further distance from the wall.

In streamline flow through a tube, the velocity gradient is parabolic, and the apex of this parabola (maximum rate of shear) under ideal conditions is located on the axis of the tube. For accurate measurements of the viscosity of a liquid or of the mobility and yield value of a slip, it is essential that these conditions be attained. In the case of flow through tubes, conditions of flow must be carefully selected that will induce the proper type of flow for the particular material under test. The type of apparatus most commonly used (when the force applied to the slip is obtained entirely from the hydrostatic pressure of the slip in the apparatus) is suitable only for slips within a narrow range of consistencies.

This objection is eliminated by the method of withdrawing a neutral solid object from the slip. During the withdrawal of a solid plate or rod from a slip, the adhering layer will be torn from the main reservoir of slip at the point of maximum rate of shear. The point is determined by the velocity of withdrawal as well as by the flow properties, surface tension, and density of the slip. These characteristics automatically combine to fix the conditions of flow so that the dimensions of the apparatus are simply a matter of experimental convenience.

The method of withdrawing a neutral solid surface from a slip and measuring the thickness of the adhering layer seems to offer attributes which are desirable in a glaze-slip test method. The method has a wide range, and the results are the effect of the integration of the various slip properties as a result of the simultaneous response of the slip to the forces applied during dipping.

The thickness of the coating of glaze on ware has been reported by Bennett[6] to be a satisfactory test of

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sponding shearing stresses. The magnitudes of these values, in fact, are less than the precision of the usual type of consistometer. These facts are of interest because they complete the picture of the flow-stress curves of slips. They also demonstrate that, when an object is being coated with slip, an adsorbed layer of water develops and forms the wet bond between the object and the slip. The thickness and characteristics of the adsorbed water film will depend on the nature and concentration of the ions in the system.

[2] V. H. Stott, D. Turner, and H. A. Sloman, "Effect of Thermal Treatment of Glass by Precise Viscometry," *Proc. Roy. Soc.*, **112**, 499 (1926); *Ceram. Abs.*, **5** [10] 305 (1926).

[3] F. S. Goucher and H. Ward, "Problem in Viscosity: Thickness of Liquid Films Found on Solid Surfaces Under Dynamic Conditions," *Phil Mag.*, [6], **44**, 1002–14 (1922); *Ceram. Abs.*, **2** [5] 113 (1923).

[4] Harold Jefferys, "Draining of a Vertical Plate," *Proc. Cambridge Phil. Soc.*, **26**, 204–205 (1930).

[5] John Satterly and H. Givens, "Shape of a Liquid Film Draining on a Vertical, Clean Wetted Glass Plate and Combined Effects of Gravity, Viscosity, Surface Tension, and Evaporation on Same," *Trans. Roy. Soc. Can.*, Series III, **26**, 145 (1933).

[6] A. L. Bennett, "Special Depth Gauge for Measurement and Control of Ceramic Coatings," *Jour. Amer. Ceram. Soc.*, **12** [9] 572–76 (1929).

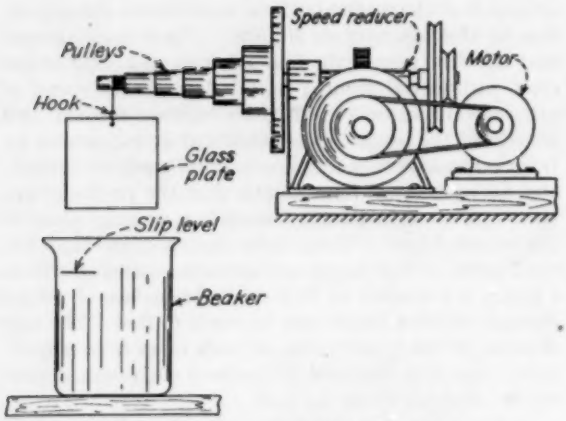

FIG. 2.—Coherence test apparatus.

glazing. In some enameling plants, slips are tested by finding the weight of slip picked up by a sheet of metal when dipped, but no attention apparently has been given the rate of withdrawal in such cases. Enamels are always applied to impervious metal surfaces, whereas no such standard surfaces are used in the glazing process. It therefore remains to be determined whether a satisfactory correlation would exist between the amount of slip picked up by a standard impervious surface and by the body to be glazed.

II. Experimental Details

(1) Scope

On the basis of the foregoing considerations, the adaptability of the "pickup" method to glaze-slip control was examined. The purpose was not to determine absolute values but rather to investigate the possibilities of the method for glaze testing. The work was done with Bristol glazes because, in general, they are the most difficult to apply correctly.

Slips were prepared from a typical Bristol glaze as a base, using different types of raw clay as follows: (1) Tennessee ball clay No. 5, (2) Tennessee ball clay No. 7, and (3) a highly colloidal Texas clay. Slips of varying characteristics were made by changing the raw clay, the water content, the electrolytes, and the aging period. The tests included (*a*) weight of glaze picked up by a standard glass plate when withdrawn at a standard uniform velocity (coherence test), (*b*) surface tension, (*c*) thickness of glaze on test tile, and (*d*) appearance of the dipped specimen after firing.

(2) Coherence Test

This test was made by immersing a glass plate in the slip, withdrawing it at constant speed, and weighing the amount of adhering slip. Adequate steps were taken to prevent errors resulting from settling by proper timing and stirring, in cases where this was important. The coherence test apparatus, shown in Fig. 2, is simply a series of pulleys of different diameter fastened to the face plate of a speed reducer driven by a small motor. By hooking a small chain to a pulley, the glass test piece can be drawn upward with a velocity depending on the diameter of the pulley.

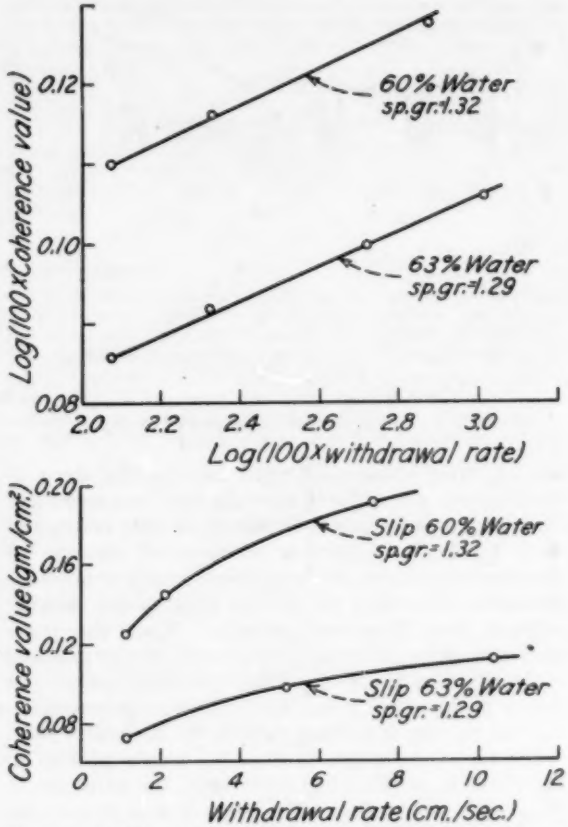

FIG. 3.—Relation between amount of slip picked up by a glass plate (withdrawn from a slip) and rate of withdrawal.

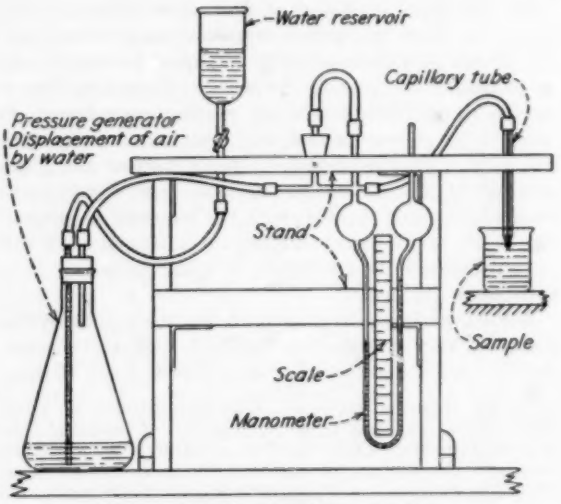

FIG. 4.—Surface-tension apparatus.

The test plates were ordinary window glass, cut as closely as possible to 3-in. squares. A small loop of fine copper wire was cemented to the top center with waterproof glue, and a wire hook was used to fasten the plate to a brass chain and later to suspend the plate from the balance arm for weighing.

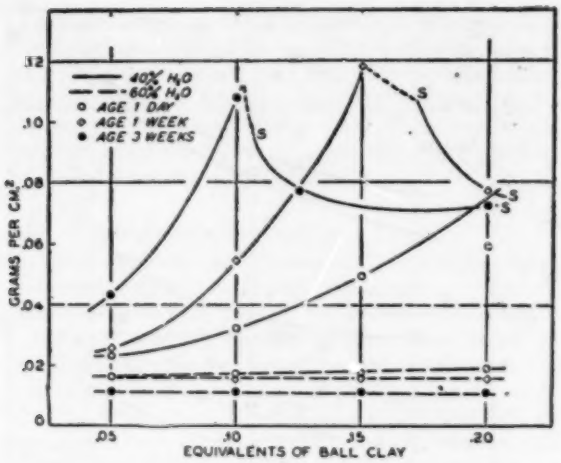

FIG. 5.—Coherence-value curves for glaze slips containing Tenn. ball clay No. 5.

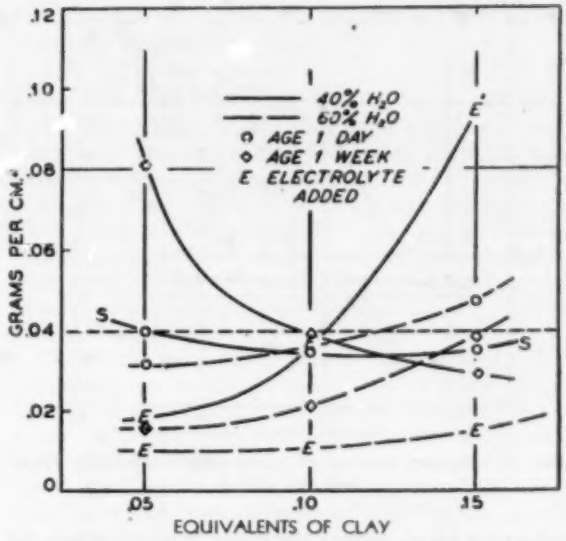

FIG. 6.—Coherence-value curves for glaze slips containing Texas clay.

The plates were cleaned by washing with fine scouring powder and sodium oleate, followed by rinsing with distilled water and drying.

The test plate was lowered into the slip and allowed to remain at rest one-half minute before starting the motor. As the bottom edge of the plate left the surface of the slip, the motor was shut off, and the plate was transferred to a balance for weighing.

The data in Fig. 3 show the log of the coherence value to be a linear function of the log of the rate of withdrawal, at least for these two slips.

The lowest available speed was used in subsequent tests, inasmuch as the precision of tests made at high velocities was likely to be impaired as a result of drainage of excess slip.

(3) Surface-Tension Test

It was thought likely that surface-tension data would be necessary to interpret properly the "pickup" data of slips. A simplified, maximum bubble-pressure apparatus was used for this test (see Fig. 4). A detailed description of a more elaborate apparatus has been given elsewhere.[7]

(4) Thickness Test

The thickness of glaze adhering to a piece of ware dipped in the slip was believed to be one of the final criteria by which the working quality of the slip may be judged. According to Bennett,[8] an Ames dial is satisfactory for this measurement. The object of this test was to find whether it is feasible to correlate the thickness of glaze deposited on a body with the amount of glaze picked up by withdrawing the glass plate as a measure of the working quality of the slip.

The apparatus used for the thickness test consisted essentially of an upright stand supporting a stage on which were two upright locating pins to hold the test tile in place. An Ames dial was firmly mounted above the stage.

To measure the thickness of glaze, a test tile was placed on the stage under the Ames dial and a reading was taken. The tile was removed, the glaze was brushed off the spot on which the gauge rested, then replaced, and another reading taken at the same spot; the difference between the two readings was considered to be the thickness at that point.

(5) Dipping Test Tile

Following the coherence test, two bone-dry stoneware test tile were dipped in each sample of glaze. The surface of the tile was brushed with a damp sponge to remove dust. The dipping was done by hand, and a standardized technique was carefully observed. Two sets of tile were dipped in each slip. The dipping time was five seconds for one set and twelve seconds for the other.

(6) Firing Test Pieces

The dipped tile were fired in a downdraft oil-fired kiln at cones 6 to 7.

III. Results

(1) Coherence Values

Typical examples of the coherence values of slips with varying water and clay contents are shown in Figs. 5 and 6. As the "thickness," or "viscosity," of the slips was increased, their coherence values increased to a maximum then diminished rapidly. This maximum coherence value was not the same for all slips but was characteristic of a given slip.

The maximum coherence effect is clearly illustrated by the curves of the slip samples that were one week and three weeks old (see Fig. 5). The portions of the curves beyond the maximum points are marked by the letter *S*. This coherence-value peak, or maximum

[7] C. W. Parmelee and C. G. Harman, "Surface Tensions of Soda-Lime-Silica Melts, II," *Univ. of Illinois Eng. Expt. Station Bull.*, No. 311, pp. 29–47 (1939); p. 31; *Ceram. Abs.*, **18** [11] 295 (1939).

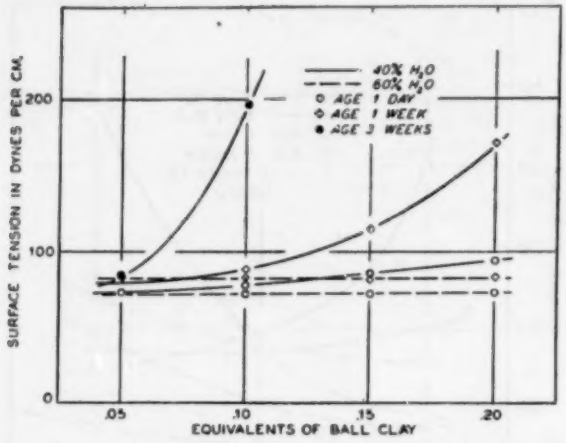

FIG. 7.—Surface tension of glaze slips containing Tenn. ball clay No. 5.

coherence value, defines the upper limit for which the coherence test can be used for a particular slip. Because stresses necessary to cause actual flow increase with "rigidity" or "thickness" of slips, the adhering layer will be torn from the main reservoir of slip at the point of maximum rate of shear. This point is determined by the rate of withdrawal of the plate and the properties of the slip. Inasmuch as the rate of withdrawal of the plate was constant in these tests, it is evident that slips having a resistance to flow greater than a certain fixed value cannot be properly tested by this method. When the plate is pulled out of such slips, a layer of slip is literally "torn" out of the slip, and very little flow occurs other than at the point of rupture.

Slips having consistencies greater than the "maximum coherence" were not well suited for application as glazes; they were not only too thick but had the characteristic of being "livery" or "clabbery." Curves representing such slips have negative slopes when plotted as in Figs. 5 and 6. The region in which the slope changes from positive to negative values is shown by two of the curves of Fig. 5. The curves in Fig. 6 having negative slopes indicate that these slips were too thick at all stages for the measurement of their coherence values and were unsuitable for glaze slips.

The effect of a deflocculating electrolyte on the coherence values of slip is shown in the curves marked *E* in Fig. 6. The curves for slips containing 40% of water and no electrolyte have negative slopes, showing that the consistencies are beyond the maximum coherence point. These slips were thick and livery and gave poor results when applied to the body. The addition of a small quantity of sodium hydroxide restored the slips to good condition by eliminating the liveriness, thinning out the slips, and moving the curves to the left of their maximum point of coherence.

The accuracy of the measurements of coherence values was not great, and no attempt was made to determine the precision of the tests inasmuch as the tests and apparatus were mainly exploratory in nature. There is little reason to doubt that these data can be

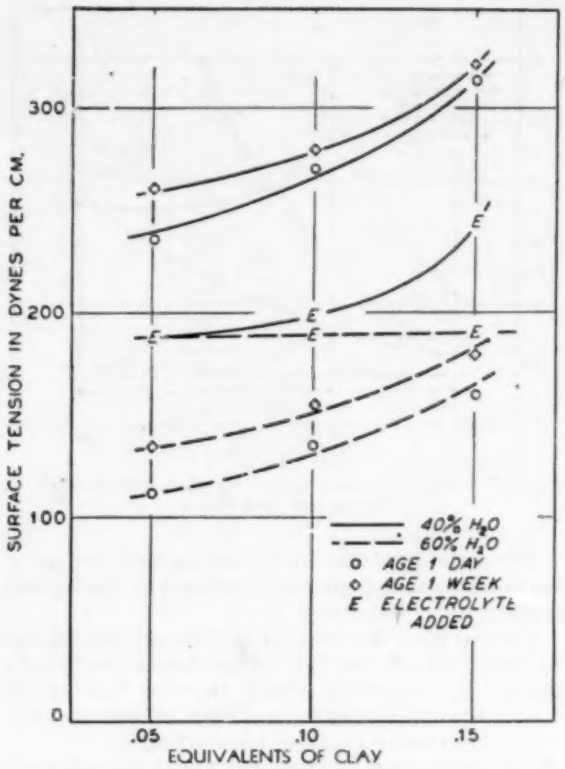

FIG. 8.—Surface tension of glaze slips containing Texas clay.

readily measured with sufficient precision because, even with the crude methods and apparatus employed for this work, most of the points lie on a smooth curve and there were few wild values. None of the observations were thrown out, and each point plotted represents an individual observation.

(2) Surface Tension

The surface tensions measured varied from 50 dynes per cm. to above 320 dynes per cm., the limit of the apparatus.

The results of surface-tension tests of glaze slips containing Tennessee ball clay No. 5 are shown in Fig. 7. With constant water content, the surface tensions increased with increasing clay content; and with constant clays, the surface tension decreased with increasing water content. The effect of varying water and clay contents and of aging time was slight for slips of good glazing consistency. These variables brought about rapid changes of surface tension only in slips outside the range normally used. The use of different clay or of electrolytes seems to have a more important bearing on surface tension. Comparison of the values shown in Fig. 8 with those in Fig. 7 illustrate the specific effects of clays and electrolytes on surface tensions of slips. The only difference between the two slips shown in Figs. 7 and 8 is in the kind of clay used Figure 8 shows that the effect of a constant percentage of NaOH is quite marked.

Surface tensions proved to have little significance for Bristol glazes applied to bone-dry bodies because the absorbent body sets up the glaze very quickly. Slips with low surface tensions had less tendency to pull away from edges and corners than others, but no conclusions could be drawn regarding the effect of surface tensions of the slip on pinholing.

(3) Thickness of Application

The thickness of the glazes on the test tile, in general, increased with increasing coherence values. The dipping qualities of the slips were definitely related to their coherence values. Successful dipping was almost impossible with slips having coherence values above 0.06 gm. per sq. cm. Samples could be dipped fairly well in slips with coherence values between 0.06 and 0.04 gm. per sq. cm., but the glaze was likely to be uneven. The resulting coating was thick, with some pinholes and poor adherence. Good dipping could be accomplished readily with slips of coherence values below 0.04 gm. per sq. cm. The use of slips with coherence values of less than 0.01 gm. per sq. cm. resulted in glaze coatings of insufficient thickness.

(4) Fired Specimens

The fired glazes showed that quite a distinct coherence value separated the good glazes from the bad. This value was 0.04 gm. per sq. cm. for the particular body employed. A total of 110 pieces was fired; of these, 52 pieces were glazed with slips having coherence values above 0.04 gm. per sq. cm., but only three test pieces could be termed satisfactory. Almost all showed more or less crawling caused by cracking as a result of too thick application.

The remaining test pieces were glazed with slips having coherence values of 0.04 or below. They were, for the most part, evenly coated and free from defects. Only nine specimens were defective in any way; three of these were close to the 0.04 gm. per sq. cm. limit; and the other six showed pinholes and minor crawling, which might have been caused by the manner of application.

II, CORRELATION OF GLAZE THICKNESS WITH AIR PERMEABILITY*

By C. G. Harman and M. K. Blanchard

Abstract

An attempt was made to correlate the thickness of deposition of glazes with the air permeabilities of the bodies. The correlation was satisfactory under certain restricted conditions but not for general cases. An adequate correlation was obtained, independent of the type of body, between thickness of glaze deposition, glaze consistency (coherence value), and water receptivity.

I. Introduction

This investigation was directed toward the satisfactory application of the coherence test, in conjunction with measurable body properties, to the more general problems of glaze-slip behavior and control.

II. Body Permeability and Thickness of Application

(1) Preparation of Samples

Clay test samples were prepared from a series of eleven mixtures of North Carolina kaolin and Tennessee ball clay so that individual blends varied systematically in increments of 10% of one of the clays. Each of the eleven mixtures was made plastic and formed by pressing in plaster molds. Three similar sets of specimens of stoneware clay were also prepared by slip casting and by soft-mud and stiff-mud consistencies in the same molds. These samples, in the dried and fired states, furnished an extremely wide range of permeabilities for testing the relation between body permeability and thickness of glaze application.

Each of these bodies was dipped by means of a mechanical dipper in the same glaze slip, and the thickness of the resulting glaze deposition was measured. The results showed good correlation between thickness of glaze deposition and the permeabilities to air for bodies of similar texture. There was a lack of correlation, however, even for bodies of the same composition which were formed by different processes. The correlation also failed for bodies formed by the same process but composed of radically different materials.

Although there was a definite usable relation between the equilibrium values for permeability to air and the amount of glaze adhering to a given body, the method was not applicable to a generalized prediction of the dipping character of all of the bodies.

III. Water Receptivity, Coherence Values, and Thickness of Application

(1) Water Receptivity

Because general correlation between body permeability to air and glaze pickup of the bodies could not be obtained, a more direct method of approach was used, namely, the measurement of the initial rate of water absorption through the body surface as related to its effect on the dipping behavior of glazes of varying consistencies.

To determine the initial rate of absorption by the test specimen, the quantity of water absorbed through a fixed body area in a given time was measured. The determination was made by measuring the gain in weight of a dry test piece which had been dipped in dis-

* See star (*) footnote, p. 202.

(1944)

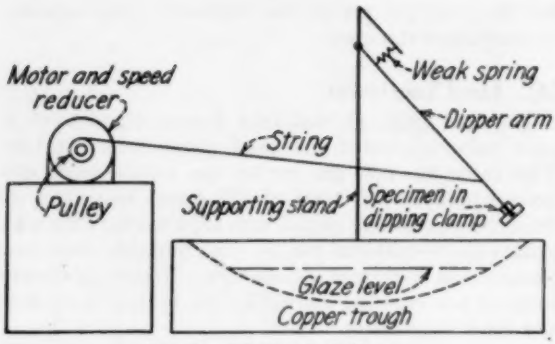

FIG. 9.—Mechanical dipper.

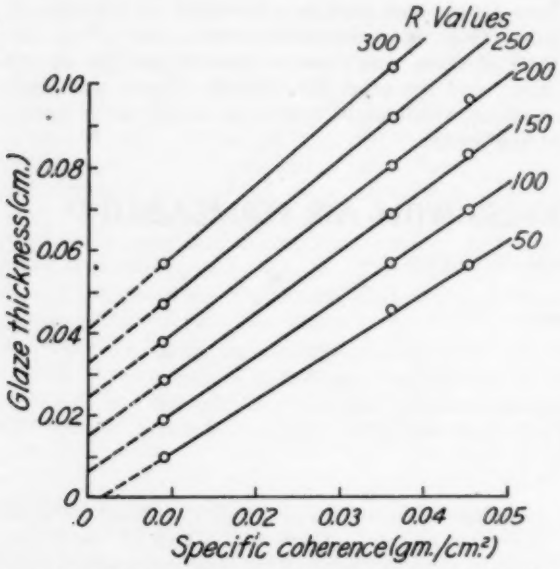

FIG. 10.—Glaze thickness as iso-R function of specific coherence; 0.05 equivalent of clay.

tilled water for five seconds. The test piece, paraffined around a standard area, was dipped by means of the mechanical dipper (Fig. 9). The weight in grams of water absorbed per square centimeter of body surface in five seconds was designated as the water receptivity, or R value, for the body. To eliminate the fractional nature of the value, each figure was empirically multiplied by 10^4, and the consequent whole numbers are used throughout as the R values.

(2) Preparation of Body Samples and Glaze Slips

To obtain test pieces with relatively low initial absorption rates, the raw samples (previously described) were fired to cone 7. This firing gave a gradation of absorption rates dependent on the quantities of the two clays present and on the consistency of the body during forming.

A Bristol glaze of constant ceramic formula was used, but varying amounts of raw clay and water were used in the slips. One slip contained 0.05 equivalent of raw Tennessee ball clay No. 5 and the other 0.15 equivalent. Both slips were milled with 50% of water for

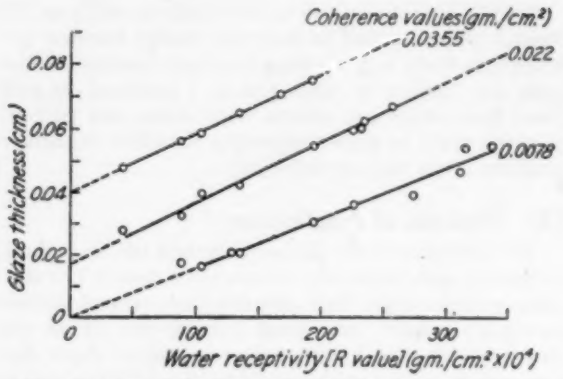

FIG. 11.—Glaze thickness as influenced by water receptivity of body and specific coherence value; 0.15 equivalent of clay.

20,000 revolutions in laboratory ball mills. Slips of three different consistencies, low, medium, and high coherence values, were prepared from each of the two original samples. The physical condition of the slip at each of these values was, respectively, thin, medium, and thick. The specific coherence values were varied by additions of electrolyte to the two base slips. To eliminate errors arising from the use of a single electrolyte, coherence values were obtained on glazes thickened by additions of $BaCl_2$, $MgSO_4$, and acetic acid and thinned by additions of distilled water or sodium carbonate.

(3) Dipping Procedure

The procedure in this set of experiments was to dip a series of raw and fired test bodies of varying R values in slips of varying consistencies for three seconds, using the mechanical dipper. Three sets of data were obtained for each of the two glazes used (0.05 and 0.15 equivalent of clay), and each glaze was set at three different consistencies or coherence values.

(4) Results

There was a linear relation, at isocoherence, between the water receptivity and the weight and thickness of glaze application (characteristic examples of these data are shown in Figs. 10 and 11). The families of curves for the low raw-clay glazes and for the high raw-clay glazes differ chiefly in the magnitude of the respective values and slightly in slope.

Examination of the glost samples revealed clearly the tendency of the glazes to crawl in the regions of high glaze weight and high body R value. Bisqued samples as well as the raw pieces were used for dipping in the same glaze, and they appear in the various graphs with the same linear relationship to R value as is noted for the raw specimens. This evidence lends weight to the generally accepted idea that most glaze defects, within reasonable limits of variables, occur as a consequence of improper weight of application.

An application of families of curves, such as those of Fig. 10, may be illustrated by an example: It is desirable to have a given weight or thickness of glaze on a given body. After a simple measurement of the R

value of the body, the specific coherence value may be read from the proper graph at the point of intersection of the desired ordinate of glaze thickness or weight with the determined iso-R value. This value of specific coherence may then be used as a positive method of glaze-slip adjustment and control with a high degree of precision.

A mathematical statement could be developed, expressing the application behavior of any glaze as a function of several simple glaze and body constants. It may be possible to use the slopes of curves to predict the desired fineness of grinding or the necessary raw clay content of a glaze slip.

Although the data for the specific glazes and bodies studied do not justify all-inclusive generalizations, they show that the applied simple tests are of definite fundamental value in the quantitative control of glaze slip.

III, ADDITIONAL GLAZES AND IMPROVED TECHNIQUE AND APPARATUS*

By C. G. Harman and H. C. Johnson

Abstract

Additional types of glazes were studied and improvements in technique and apparatus are described. The correlation between glaze consistency, body receptivity, and thickness of deposition is represented by a simple first-order equation having two constants, $P = K\left(\frac{R}{100}\right)(C - 0.001)$, wherein P = pickup, K = deposition constant, R = receptivity, and C = coherence value.

I. Introduction

The principles and development of the coherence test have been described in Part I.† The weight of slip cohering to a unit area of the glass plate was called the coherence value and expressed the consistency of the slip. Part II‡ has dealt with correlation of the thickness of deposition with the air permeabilities of the bodies and the consistency of the slip measured by the coherence method. The correlation was satisfactory only when bodies of a single type were compared. To find a more general method of estimating the affinity of a body for a glaze coating, the bodies were dipped for five seconds in distilled water and the gain in weight was measured. The amount of water absorbed by the body per unit area during this operation was termed the "receptivity value" of the body and referred to as the R value. Good correlation was shown by plotting the R value of various bodies against the thickness of glaze coatings for slips of constant coherence value. By this means, the slip consistency (coherence value) required to give the desired glaze coating for a body of any receptivity could be found and maintained and thus keep glost defects to a minimum.

The present investigation, Part III, was undertaken primarily to determine whether or not the same methods could be applied successfully to other types of glazes. An additional objective of this work was to improve the technique and apparatus.

II. Measurement of Body Receptivities, Slip Coherence Values, and Body Glaze Pickup

(1) Body Samples

The bodies used in this work, listed in Appendix A, p. 211, were fired to more than one temperature in most cases to give several samples of varying R values.

(2) Significance of Time Element in Determining Receptivity and Thickness of Glaze Application

The R-value measurement was adopted to find a readily measurable property of bodies which would designate the affinity of a body for a glaze coating. This value was determined by finding the weight of water absorbed per unit area when the body was dipped in water instead of glaze. (It was necessary to use water instead of glaze to have a dependable standard.)

In the first experiments on receptivity, a constant area of body was carefully exposed to the water; this practice has since been found unnecessary and possibly undesirable. In early experiments, an arbitrary dipping time of five seconds was used for receptivity determinations and another arbitrary dipping time of three seconds was used for applying the glaze. The reason for the longer dipping time for the receptivity tests was to increase the weight of water absorbed and thus to reduce the percentage error from weighing.

Curves obtained by this procedure do not conform to the ideal inasmuch as considerable glaze deposition is indicated for bodies having a receptivity of zero. The ideal curve would be expected to extrapolate to the origin; this fact is obvious because a body with no affinity for the glaze would retain none.

The procedure of using a longer dipping time in water for receptivity values than in glaze for glaze pickup merely shifts the curves from their true positions. The extension of a family of these curves should converge at the left of the origin because a longer time of exposure was used during the measurement of the receptivity. These dipping times would be justified only on the basis of convenience.

The results now to be presented were obtained by using equal dipping time for R values and glaze pickup. The type of curve obtained by this procedure is shown in Fig. 12. To obtain the spread in R values for these

* See star (*) footnote, p. 202.
† See this issue, pp. 202–207.
‡ See this issue, p. 207.

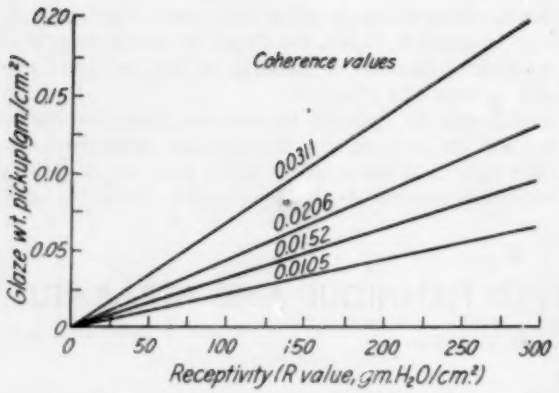

FIG. 12.—Type of curves obtained when same dipping time is used for both receptivity and pickup tests.

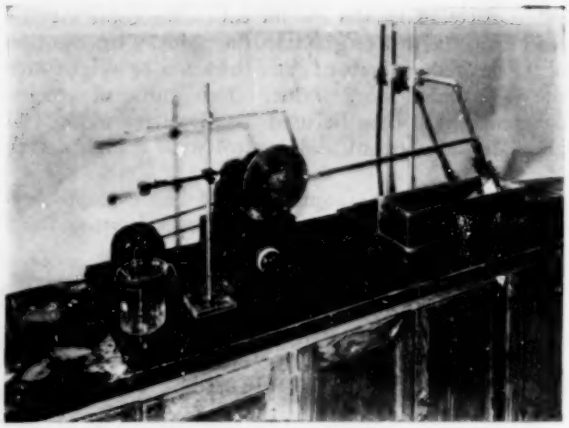

FIG. 13.—Apparatus for measuring coherence values and body receptivity.

data, a full series of bodies (see Appendix A, 211) was used.

(3) Apparatus and Procedure

Best results are obtained with a standardized dipping speed (glass plate and test pieces) and a standardized depth of immersion. Satisfactory results, however, can be obtained at several dipping speeds if the time of contact of the sample with the water for R values is the same as with the glaze for glaze pickup. Better checks are also obtained on coherence values when a standard time and depth of immersion of the glass plate are used.

Control of immersion time was conveniently met by means of the apparatus shown in Fig. 13. Data obtained by means of this apparatus were found to check with those obtained by previously used procedures.

In making the coherence test, the beaker shown at the left in Fig. 13 was filled to definite height with slip. The cleaned glass plate was weighed and fixed in place as shown, and the motor was started, causing the plate to be immersed in the slip and withdrawn. The plate with its cohering layer of slip was again weighed. The weight of slip per square centimeter was termed the coherence value of the slip.

The receptivity and glaze pickup measurements were made by means of the apparatus shown at the right side of Fig. 13. For receptivity determinations, the rectangular copper vessel at the right was charged with a fixed quantity of water. The dried and weighed body sample was then clamped in place. After a sweep across the surface of the water, the sample was again weighed. The R value was taken as the weight of water ($\times 10^4$) picked up per square centimeter of the test body surface in a standard dipping time. All of the receptivity data have been multiplied by 10^4 to eliminate cumbersome decimals.

Glaze pickup was determined in exactly the same manner as receptivity except that glaze was used instead of water; it is the weight of dry glaze deposited per square centimeter of body surface dipped in the slip for a standard length of time.

For making R-value and glaze-pickup tests, it was necessary to have the test pieces dry and approximately at room temperature. The test pieces were taken from the drier and cooled in a desiccator over calcium chloride until ready for use. It was noted early in this investigation that sulfuric acid, when used as the desiccant, was adsorbed on the surfaces of the test pieces and greatly affected glaze pickup.

III. Results with Different Types of Glazes

(1) Method of Representing Data

(*A*) *R-Value versus Glaze Pickup Curves:* The best correlation between the body and the glaze slip was obtained by determining the coherence value of the glaze, the glaze pickup, and the R value of the body. These data were plotted as R value versus glaze pickup for single slips of constant coherence value.

The data are shown graphically in the figures which follow; the individual points were plotted on the curves to illustrate the accuracy and reliability of the data. At high values of coherence and receptivity, there is considerable variation. The points falling off the curves generally represent samples that were badly pinholed, and they usually lie outside the range of practical operation.

In Figs. 14, 16, 18, and 20, in which glaze pickup is plotted against R values, each curve represents the data for a single slip of constant consistency. Changes of slope or breaks in these curves indicate changes in the deposition phenomena. The breaks and the rate of deposition beyond them are related to the deposited coatings because the lines beyond the breaks in each case are crudely parallel. The rate of deposition beyond the break is controlled by the permeability of the deposited glaze layer rather than the body receptivity or by a combination of the two together with a clogging of the pores of the body. The phenomena associated with the breaks in the curves do not restrict this method of testing but broaden its scope.

Observations of the glazed specimens, both in the raw and fired condition, invariably showed that defective glazes predominated on specimens glazed under

Appendix A: Body Compositions

Body No.*	Tenn. ball clay No. 5 (%)	N. C. kaolin (%)	Body No.	Tenn. ball clay No. 5 (%)	N. C. kaolin (%)	Stoneware clay: Whitehall stoneware†	Stoneware clay: Consistency
1	100		7	40	60	A	Very stiff
2	90	10	8	30	70	SM	Medium stiff
3	80	20	9	20	80	B	Jiggering
4	70	30	10	10	90	SO	Very soft
5	60	40	11		100	C_{WH}	Casting
6	50	50					

* Plastic process; fired to cones 8 and 5; marked 11–1, etc.
† Bodies A and B fired to cone 8; bodies SM, SO, and C_{WH} fired at both cones 8 and 5; marked SM–1, etc.

	Sanitary ware: Body C	Sanitary ware: Body D	High-tension insulator (body E)	Hotel china (body F)	Semivitreous dinnerware (body G)	Porcelain (body H)
A 1 china clay	20.0					
Quartz flint	35.0	17.7	19.0	35.0	35.0	
Keystone feldspar	19.0	32.6		21.0	13.0	40.0
Whiting	1.0					
Fla. kaolin	10.0	4.7				18.0
Tenn. ball clay No. 5	10.0	7.0				
Whiteway English ball clay	0.5					
Ga. kaolin		26.3	35.0			27.0
Ky. ball clay No. 4		7.0				
Fla. ball clay			6.0	13.0	12.0	
N. C. kaolin		4.7				
No Karb ball clay			11.0	20.0	12.0	
Ky. Old Mine ball clay No. 4			28.0	9.5	18.0	
Talc			1.0			
Dolomite				1.5		
Ky. ball clay No. 12					10.0	
Flint						15.0
Fired to (body No.)	Cone 5(C–1) Cone 4(Cn)	Cone 4; some pieces refired to cone 9	Cone 4; some pieces refired to cone 9, some to cone 10	Cone 4; some pieces refired to cone 9	Cone 4; some pieces refired to cone 9	Cone 4; some pieces refired to cone 9, and some to cone 10
Batch preparation		Casting (7000 gm.)	Plastic process (7000 gm.)	Plastic process (7000 gm.)	Slip cast (10,000 gm.)	Slip cast (10,000 gm.)

Appendix B: Glaze Compositions *

	Bristol glaze: Glaze B 3	Bristol glaze: Glaze C 1
0.25KNaO, 0.45CaO, 0.30ZnO } 0.5 Al_2O_3 3.5 SiO_2		
Feldspar No. 54	44.1	
Whiting	12.7	11.09
Tenn. ball clay	8.8	
N. C. kaolin (calcined)	3.0	0.29
Zinc oxide (calcined)	7.2	5.95
Quartz flint	24.2	29.42
Ky. Old Mine ball clay No. 4		7.49
Feldspar No. 45		45.80

Raw lead glaze (L 3)		Fritted lead borosilicate glaze (F 1)	
0.9 PbO, 0.1 MgO } 0.2 Al_2O_3 2.0 SiO_2		0.43 CaO, 0.26 PbO, 0.12 K_2O, 0.06 Na_2O, 0.13 ZnO } 0.27 Al_2O_3 { 2.6 SiO_2, 0.31 B_2O_3	
Red lead	56.3		
Heavy magnesium carbonate	2.39		
Fla. kaolin	10.96		
N. C. kaolin (calcined)	3.14		
Quartz flint	27.19		

Frit No. 1		Frit. No. 2		Total batch	
Red lead	11.21	Whiting	28.01	Frit No. 1	29.65
Whiting	5.46	Eureka spot	17.86	Frit. No. 2	29.80
Aluminum hydroxide	17.00	Borax	5.88	Whiting	0.71
Flint	65.44	Boric acid	24.61	Zinc oxide (calcined)	3.13
		Flint	23.64	Feldspar No. 54	18.50
				English china clay	4.50
				Flint	14.15

* In selecting the glaze compositions, an attempt was made to use some representative types of glazes to determine scope of usefulness of the pickup method of glaze control.

(1944)

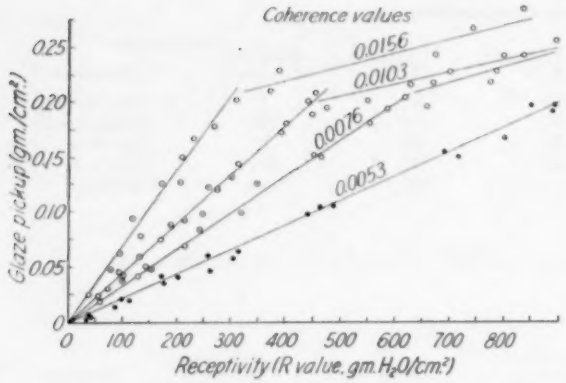

FIG. 14.—R value versus glaze pickup; Bristol glaze, B 3.

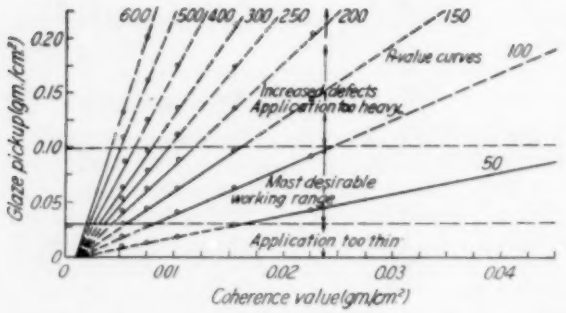

FIG. 15.—Coherence value vs. glaze pickup, iso-R line chart; Bristol glaze B 3.

conditions represented by points to the right of the break in the curve. This condition may be caused by (1) a glaze slip too thick for a given body, (2) too long dipping time for a given glaze and body, (3) too heavy application of glaze, or (4) an overmilled glaze or too much "superfine" material in the glaze. A more detailed description of these results follows.

(*B*) *Iso-R Line Charts:* The three variables, glaze pickup, R value, and coherence value, are best shown when plotted as in Fig. 15. These graphs have been called iso-R line charts because each curve of a family represents bodies of constant receptivity, which results in a linear relationship between the two empirical quantities when the receptivity of the body for glaze is constant. The iso-R line charts (Figs. 15, 19, and 21) conform to the theoretical idea that the individual curves converge on the coherence-value axis at a point designated by the coherence value of water (0.001).

Data in this form may serve as control charts for glazes with reasonable accuracy and show the deposition properties of the glaze by the slope of the iso-R line.

(2) Bristol Glaze

The results of the tests on Bristol glaze slips are shown in Figs. 14 and 15. Glazes (B 3, Appendix B) were applied to the whole set of bodies shown in Appendix A. Although bodies which are usually coated with Bristol glazes have R values between 150 and 350,

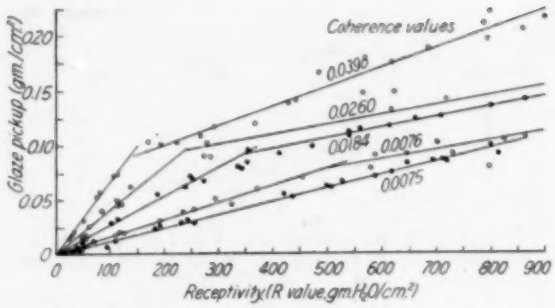

FIG. 16.—R value versus glaze pickup; raw glaze L 3.

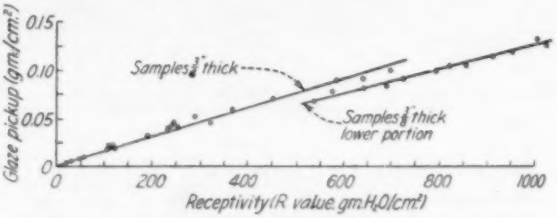

FIG. 17.—Effect of thin samples with standard dipping time; glaze L 3, coherence value of slip, 0.0076.

the experimental series was much more extensive than this.

The presence or absence of defects closely paralleled the thickness of application. Figure 15 shows the most desirable working range for application of the Bristol glaze slips to bodies insofar as freedom from surface defects was concerned.

(3) Raw Lead Glaze

Figure 16 gives the results of the tests made on a raw lead glaze (L 3, Appendix A) at varying coherence values as shown on each curve. These curves show that the amount of glaze deposited on the body during dipping may be correlated with the body condition for any given coherence value. A family of such curves illustrates how a glaze may be set up for proper application to any body.

There is a marked change in the slope of the curves when the weight of glaze deposited reaches about 0.1 gm. per sq. cm. This break has a real significance because all of the glazes on the test pieces, represented by data to the right of the break, cracked in drying or failed to adhere to the body. No such defect appeared for conditions to the left of the break.

During the course of the investigation of these glazes, a series was found in which data taken on samples of different thickness did not check (see Fig. 17). Further investigation showed this to be caused by saturation of the surface of the test pieces and a clogging of the pores with fine glaze particles. The results of further investigation of these effects are shown in (*A*), (*B*), and (*C*) of Fig. 18. The data shown in Fig. 18 prove that the specimen thickness is of no consequence if surface saturation is not allowed to occur. The thickness of the ware has a bearing on its receptivity in extreme cases, but in such borderline cases, adjust-

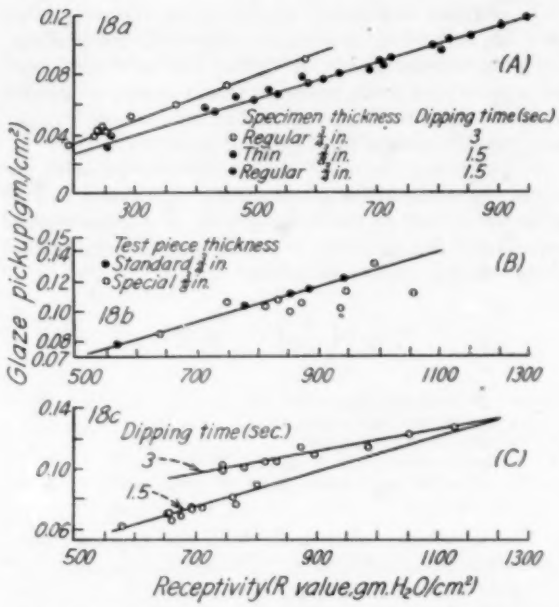

FIG. 18.—(*A*) Results showing poor correlation between thin, highly porous bodies and thicker ones at 3 seconds dipping time; good correlation at faster dipping time; coherence value of slip, 0.0075. (*B*) Surface saturation of thin test samples in standard dipping time; coherence value of slip, 0.0079. (*C*) Effect of dipping time on saturation point of thin samples; coherence value of slip, 0.0087. All samples ³/₈ in. thick.

ment of dipping time can be made in such a way as to permit good correlation even though the bodies have varying thicknesses. Except for these extreme cases, no variation of R value with specimen thickness has been noted. These data demonstrate that the consistency of glazes for dipping porous ware would probably have to be a little different for thick articles than for thin ones.

A factor of considerable importance is that of R-value variations of the ware itself. An example of such variation is shown by the R values plotted in Fig. 18 (*C*), which were obtained by using samples of commercial tile chosen at random from a single shipment. A valuable and easy method is thereby obtained to check and control the processing and forming of ceramic ware.

The iso-R line chart for the raw lead glaze is shown in Fig. 19. The area labeled "good glazes" was determined by observing test pieces in the raw and fired states. These observations were checked under conditions simulating industrial practice. The best glazes were obtained at about 0.05 gm. per. sq. cm. of glaze.

(4) Fritted Lead Borosilicate Glaze

The results of tests with fritted lead borosilicate glazes (F 1, Appendix B) at varying consistencies are shown in Fig. 20. The consistency of this fritted glaze was varied in five steps, having coherence values of 0.0300, 0.0239, 0.0127, 0.0099, and 0.0068 gm. per sq. cm. Bodies having a wide range of compositions (Appendix A) and R values were used. The slip with a co-

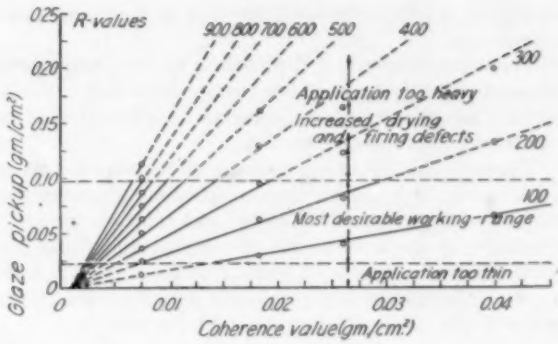

FIG. 19.—Coherence value versus glaze pickup iso-R line chart; raw lead glaze L 3.

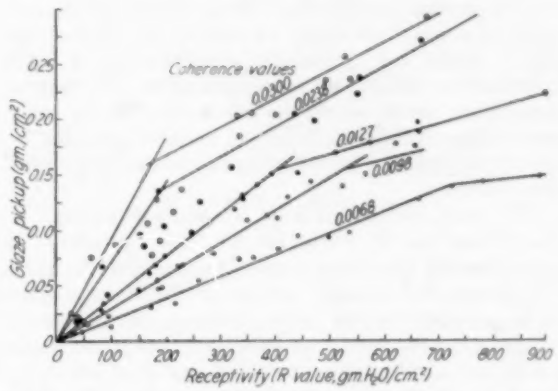

FIG. 20.—R value versus glaze pickup; fritted glaze F 1.

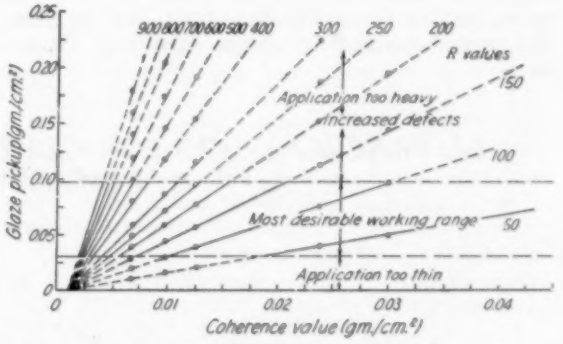

FIG. 21.—Coherence value versus glaze pickup, iso-R line chart; fritted glaze F 1.

herence value of 0.0300 was very thick and was satisfactory only for application to bodies with an R value below 100. Because fritted glazes are deposited more rapidly on bodies than some other types of glazes and because this glaze was very thick, small experimental errors were magnified. Such scattered distribution of points indicates clearly that this slip did not possess a consistency which would permit its uniform application except possibly for highly vitrified bodies.

A somewhat thinner slip with a coherence value of 0.0239 can cover a wider range of bodies and the points are not so badly scattered. When the slip was thinned

to 0.0127, a much smaller dispersion of points was obtained.

The coherence values diminished as the glazes were thinned and the slopes of the curves decreased. For a given glaze, the slopes of the curves are proportional to the coherence values of the slip.

The iso-R line chart for fritted lead borosilicate glaze slips in Fig. 21 is similar to corresponding diagrams for the other glaze types. The general relation between thickness of application and the drying and firing defects was the same for this glaze as for the other two types. The area of acceptable glazes was between 0.03 and 0.09 gm. of glaze per sq. cm. of body surface.

IV. Application of Method and Deposition Constant

As a practical application, the iso-R line charts may serve as a basis of control for setting up glazes. The charts would vary somewhat with changes of batch constituents, but these changes should not be great because these variables are directly related to the coherence values. There is, however, a slight variation between the various types of glazes as shown by the iso-R line charts.

The iso-R line charts may be used as follows: (1) Determine the R values of the body by using the same dipping time that is used in applying the glaze. (2) Choose the desired weight or thickness of glaze to be applied to the body surface. (3) Follow the weight line horizontally on the chart until it crosses the iso-R line corresponding to the R value of the body. (4) Read off the corresponding coherence value given on the chart. (5) Set the glaze to this coherence value and dip the ware. (6) Use the coherence value as a control test to check the glaze from time to time. (7) Check the receptivity of the ware from time to time.

In addition to a control test for glazes, the receptivity test can be used to advantage in checking the uniformity of processed ware. R values will be found more satisfactory for many purposes than porosity or density measurements and may be made much more rapidly and usually with at least as great accuracy.

In preparing the iso-R charts and working with the data, the straight-line relationships were found to lend themselves well to the development of a glaze-control equation. Equation (1) is based on the accumulated data found in the iso-R charts.

$$P = K\left(\frac{R}{100}\right)(C - 0.001) \qquad (1)$$

P = glaze pickup (gm./cm.^{2}).
C = coherence value (gm./cm.^{2}).
K = deposition constant.
R = body receptivity (gm. $H_2O \times 10^4$/cm.^{2}).
0.001 = coherence value of water (gm./cm.^{2}).

This equation, when used with the proper values, will give the iso-R charts. The deposition constant* (K) for the three glazes used in this work (B 3, L 3, and F 1, Appendix B) are as follows: 4.34 for glaze B 3 (Bristol), 1.80 for glaze L 3 (raw lead), and 3.26 for glaze F 1 (fritted type).

The determination of a few accurate values makes it possible to use this equation for the prediction of the behavior of a glaze under different conditions. These data are helpful in the laboratory as an aid in studying the effects of the many variables affecting the deposition constant.

* The deposition constant defines the relation between receptivity and the coherence value of a given slip or suspension and may be said to define the rate of deposition of solids from a slip or suspension onto a body.

IV, PRACTICAL USES FOR COHERENCE VALUE AND RECEPTIVITY MEASUREMENTS*

By C. G. Harman and H. C. Johnson

Abstract

Coherence-value and receptivity measurements may be used as (1) a check on incoming raw materials, (2) a basis for selection of certain raw materials, (3) a control test for slip consistency, (4) a control test at various steps in the manufacturing process, and (5) a basis for blending clays and other raw materials. These methods also hold promise of general application in fields other than glaze control.

I. Introduction

(1) General Considerations

In Parts I, II, and III, the development of the pickup method of glaze-slip control has been studied. The method is based on a few easily measured properties, such as coherence value, receptivity, and pickup. These three simple values, when properly correlated, give a good picture of slip behavior.

The terms are defined as follows: (1) "Coherence value" is the weight of slip adhering to a unit area of glass plate immersed in a slip and withdrawn therefrom at a constant rate of 1 cm. per second. It is expressed as weight in grams of slip per square centimeter of plate area. (2) "Receptivity" is the weight of water picked up and absorbed per square centimeter surface of a test sample of ware after immersion under standard conditions. This weight per square centimeter is arbitrarily multiplied by 10^4 to eliminate cumbersome

* See star (*) footnote, 202 p.

decimals. (3) "Pickup" is the weight of solids, in grams, deposited per square centimeter area of the test sample of ware after immersion in slip under standard conditions.

The first part of this investigation was concerned with glaze slips of various types, namely, Bristol, raw lead, and fritted lead borosilicate. The method was found to work well with each of these glazes. The final stage of the work with glaze batches resulted in the preparation of iso-R charts for each glaze slip. These curves may be represented by a simple first-order equation (1) (see p. 214).

$$P = K\left(\frac{R}{100}\right)(C - 0.001)$$

This method is believed to be applicable to the study and control of any slip, and it may prove to be generally applicable to the study and control of any finely subdivided ceramic material. The present publication is a report of a preliminary examination of these possibilities.

If a testing procedure is to be generally applicable to fine-grained ceramic materials, it must be based on principles common to all such materials without regard to origin or species. The properties of slips and, to a considerable extent, those finely divided plastic and dried ceramic materials and mixtures are derived from a common set of fundamental variables. This concept permits the treatment of ceramic materials either as mixtures or individuals and provides a logical method for the study of the effects of various factors on these materials.

(2) Classification of Variables

The interrelation referred to is shown in Fig. 22. The characteristics and properties of finely divided ceramic materials may be classified in three main groups, namely, primary, secondary, and derived groups. The primary group defines composition, which includes the chemical, mineral, and physical compositions of the material. Chemical composition, of course, is defined by the chemical analysis of the substance. Mineralogical composition refers to the identity and proportions of the various natural or artificial species that may be present, which includes natural or artificial crystalline, amorphous, or glassy phases. Physical composition specifically refers to particle sizes and particle-size distribution of the individual mineral constituents.

The factors in the primary group are of basic importance and are responsible for the identity of the material. They are fixed for any given material, and no reversible change is possible in any of them. They are not influenced by any of the factors of the other two groups but are the controlling factors in fixing the properties in the secondary group and in the derived group.

The factors in the composition group are, however, subject to alteration by temperature, water, chemical treatment, and mechanical treatment. The changes in the compositions brought about by these treatments are fully transmitted to the secondary group and are duly reflected in the properties of the derived group.

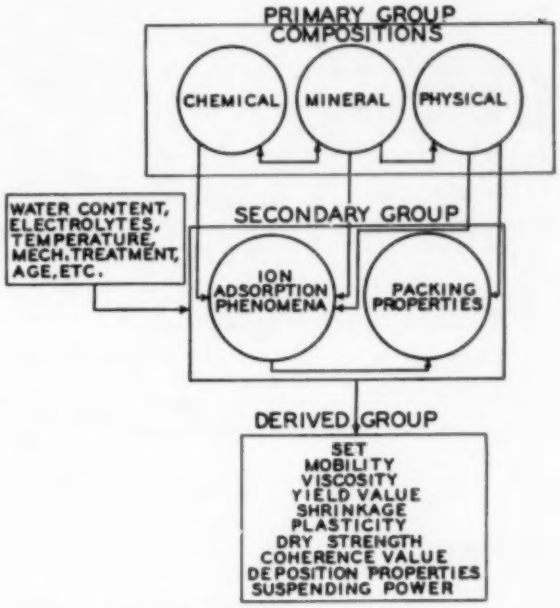

FIG. 22.—Chart of relationships.

Most of the properties of general significance are derived, not directly from the compositions but from the secondary group, as shown in Fig. 22. The secondary group may be considered to integrate the particle-size distribution curves and to transform the chemical energies of particle surfaces into more flexible form. The conception of the secondary group makes it possible to consider the combined effect of particles of all sizes and all kinds in simple and usable form. Without this concept, it would be necessary to deal with the hopeless case of the detailed data concerning the character of individual particles.

The secondary group is composed of adsorption and surface effects and of the packing characteristics of the particles. Ion adsorption involves what is sometimes loosely termed "base exchange." It is this property of small particles that is responsible for their sensitivity and responsiveness to electrolytes. The packing characteristics of the particles are responsible for the porosity and permeability and have a direct influence on several of the properties of the derived group.

The properties in the derived group are usually those of most direct interest to ceramists, and some of them are listed in Fig. 22. The list could be greatly enlarged. These properties are controlled directly by the factors in the secondary group and may be widely and reversibly varied by factors in other groups and by such outside agencies as water content, time, temperature, and electrolyte.

A picture of how all of these factors enter into the preparation of a glaze slip is shown in Fig. 23. This diagram illustrates the interrelation between all the various factors involved in the preparation of a glaze slip. Similar diagrams could be constructed for other types of slips and materials. According to this diagram, the batch composition and the processing, if properly

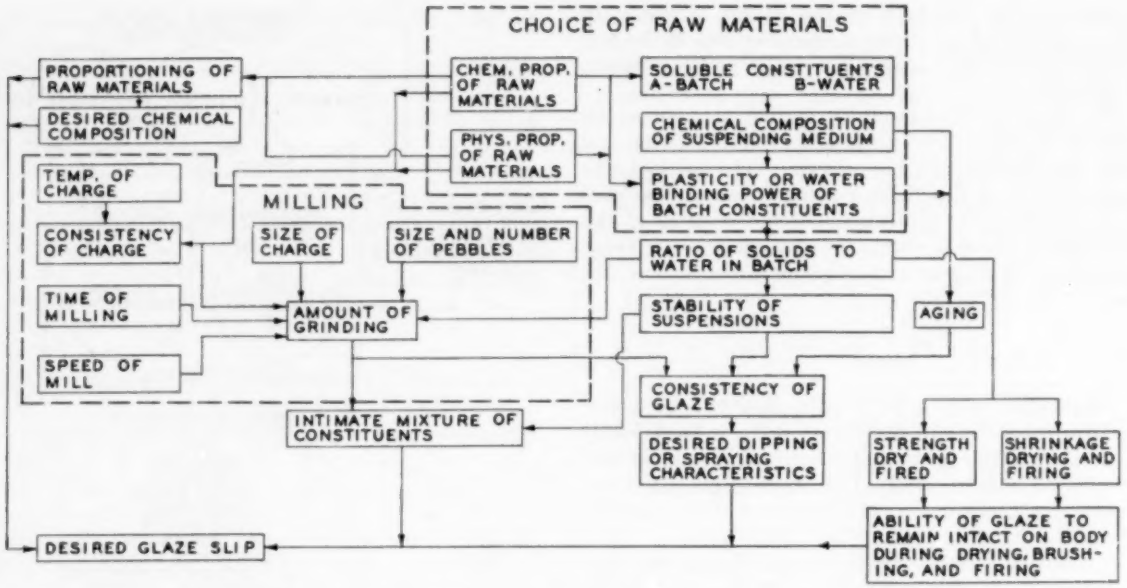
CHOICE OF RAW MATERIALS
PROPORTIONING OF RAW MATERIALS
DESIRED CHEMICAL COMPOSITION
CHEM. PROP. OF RAW MATERIALS
PHYS. PROP. OF RAW MATERIALS
SOLUBLE CONSTITUENTS A-BATCH B-WATER
CHEMICAL COMPOSITION OF SUSPENDING MEDIUM
PLASTICITY OR WATER BINDING POWER OF BATCH CONSTITUENTS
TEMP. OF CHARGE
CONSISTENCY OF CHARGE
MILLING
SIZE OF CHARGE
SIZE AND NUMBER OF PEBBLES
RATIO OF SOLIDS TO WATER IN BATCH
TIME OF MILLING
AMOUNT OF GRINDING
STABILITY OF SUSPENSIONS
AGING
SPEED OF MILL
CONSISTENCY OF GLAZE
INTIMATE MIXTURE OF CONSTITUENTS
DESIRED DIPPING OR SPRAYING CHARACTERISTICS
STRENGTH DRY AND FIRED
SHRINKAGE DRYING AND FIRING
ABILITY OF GLAZE TO REMAIN INTACT ON BODY DURING DRYING, BRUSHING, AND FIRING
DESIRED GLAZE SLIP

FIG. 23.—Control of glaze consistency.

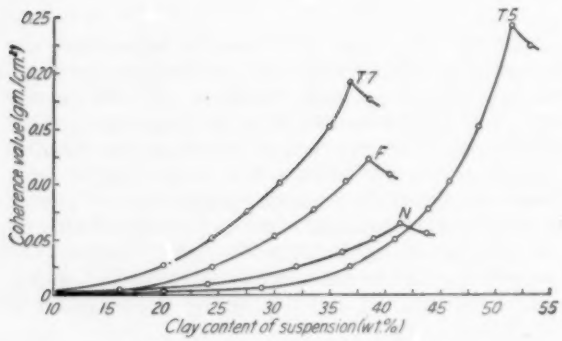

FIG. 24.—Coherence values versus percentage of solids of typical clays; *F*, Fla. kaolin; *N*, N. C. kaolin; *T* 5, Tenn. ball clay No. 5; *T* 7, Tenn. ball clay No. 7.

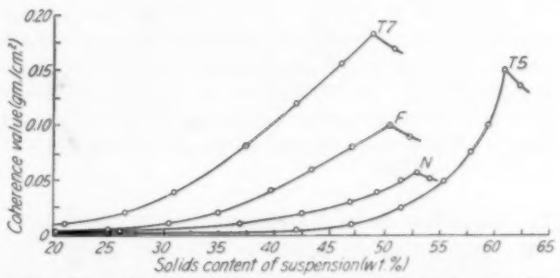

FIG. 25.—Coherence values versus percentage of solids; clays diluted with 50% flint; *F*, Fla. kaolin; *N*, N. C. kaolin; *T* 5, Tenn. ball clay No. 5, *T* 7, Tenn. ball clay No. 7.

controlled, may be widely varied and yet arrive at slips of equivalent quality. It was the purpose of this work to examine the feasibility of such control by means of the principles which have been described.

II. Tests and Test Results

(1) Effect of Water Content and Character of Solids on Coherence Values of Suspensions

(*A*) *Coherence Values of Clay–Water Systems:* The first variable to be studied was that of water content. The clay slips were prepared with as low water content as possible and milled for one hour. Such slips were barely thin enough to pour from the mill. After milling, they were diluted with successive additions of distilled water, and coherence values were measured after each dilution. Such procedure made it possible to plot coherence values against percentage of solids in the slip and to obtain the whole curve, including the maximum point.

Figure 24 shows a group of such curves for some typical clays. North Carolina and Florida kaolins and Tennessee ball clay No. 7 appear to fit in a series, whereas Tennessee ball clay No. 5 does not; the latter is the only clay of this group having an appreciable quantity of finely dispersed organic matter present. This clay made a fairly well-dispersed slip when mixed with water, whereas the slips made from the other three clays were flocculated.

(*B*) *Floating Power:* The same group of clays, each diluted with quartz flint to the extent of 50% of the dry batch weight, was made into slips with as low water content as possible, milled one hour, and diluted with successive additions of water. Coherence values were determined on the slips after each dilution. The results are shown in Fig. 25. Tennessee ball clay No. 5 suffers the greatest change (compare with data in Fig. 24) and has the lower floating power at low concentrations.

(*C*) *Coherence Values of Blended Clays:* Figures 26 and 27 are typical cross plots of coherence value-percentage solids curves, in which the components

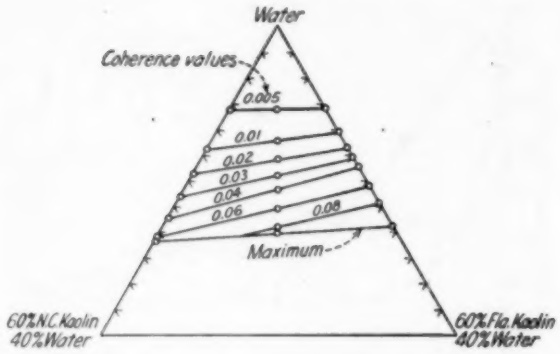

FIG. 26.—Coherence-value contours for blends of Fla. kaolin and N. C. kaolin at varying water content.

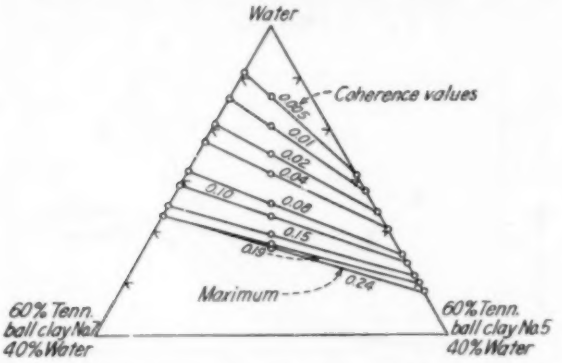

FIG. 27.—Coherence-value contours for blends of Tenn. ball clay No. 7 and Tenn. ball clay No. 5 with varying water content.

vary as shown. These figures represent the clays and water in triaxial fields on which are plotted coherence-value contours. The line labeled "maximum coherence" represents the limiting coherence value for the slips, corresponding to peaks such as those in Figs. 24 and 25. The triaxial diagrams illustrate how clays may be blended to give any desired coherence value. This blending method may be applied, for example, to impart the necessary floating characteristics to a suspension with a given amount of clay.

It should be noted that the coherence-value contours are essentially straight lines. The triaxial field can therefore be obtained simply by drawing straight lines between equal coherence values of any two curves such as those in Fig. 24.

(*D*) *Blends of Clay and Nonplastics:* To illustrate the method of correlating the data pertaining to clays with other batch constituents, triaxial diagrams were obtained for clay–flint–water systems. A typical example of the results is shown in Fig. 28. Flint was chosen for this work because it is insoluble and stable and does not release flocculating or deflocculating ions to the slip. Any other batch material could have been used by a proper accounting of the soluble salts.

(*E*) *Application:* When properly used, these triaxial curves can furnish a method of checking new batches of raw materials for constant floating properties and floating requirements as well as for other purposes. Such charts may be useful as guides for correcting the consistency of slips to satisfy definite requirements, for checking raw materials and batches, and for blending clays.

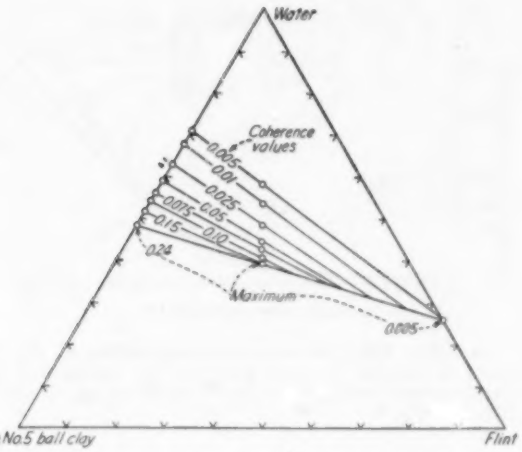

FIG. 28.—Coherence-value contours for blends of Tenn. ball clay No. 5 and flint at varying water content.

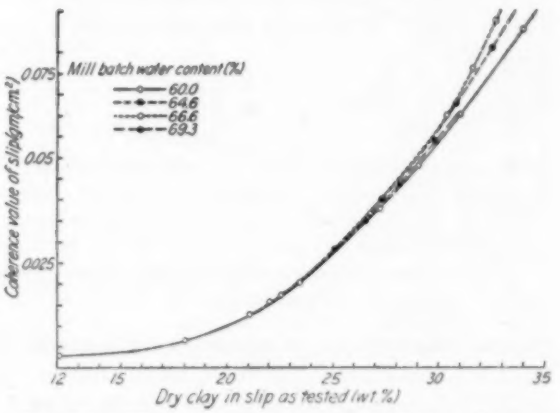

FIG. 29.—Effect of consistency on milling a slip composed of Fla. kaolin and water; water content of mill batch as indicated; water content on abscissas obtained by diluting milled batch.

The triaxial plots of consistencies of clay, flint, and water as well as the curves showing percentage of solids versus coherence values demonstrate a useful method of representing the properties of fine-grained ceramic raw materials.

The several factors entering into the slip preparation exert some effect on the properties and change the curves accordingly. Sufficient data are not available at the present time to show absolutely how these curves will be altered. Some information, however, has been obtained and is presented.

(2) Effect of Consistency on Milling

Figure 29 illustrates how the amount of grinding (in ball mills), as influenced by altering the water content of the slip in the mill, affects the coherence-value versus

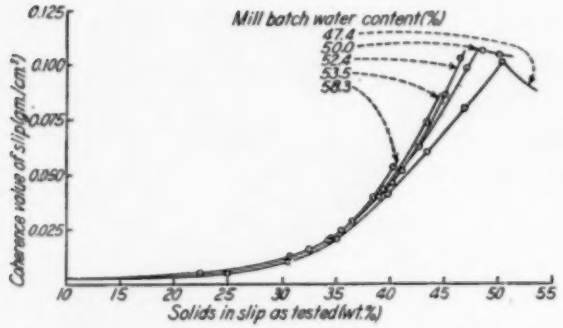

FIG. 30.—Effect of consistency on milling of slip composed of mixture of equal parts of Fla. kaolin and flint; water content indicated on abscissas obtained by diluting milled batch.

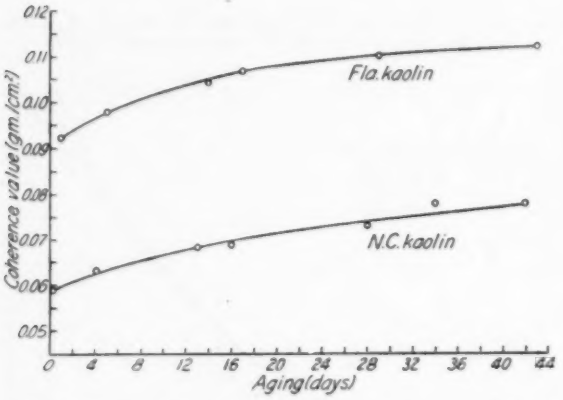

FIG. 31.—Effect of aging on consistency of Fla. and N. C. kaolin.

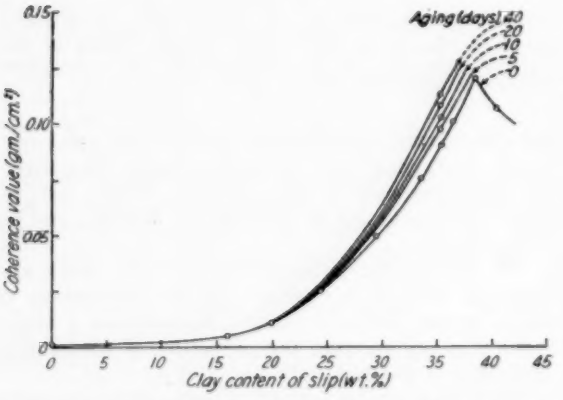

FIG. 32.—Effect of aging on consistency of Fla. kaolin.

solids curve for Florida kaolin. These data indicate that there is no marked effect on the clay. With materials difficult to slake, the change would be much more pronounced as illustrated by means of a slip composed of equal parts of Florida kaolin and quartz flint. The effect of the water content of the slip on milling was more marked in this case than with the clay alone (Fig. 30).

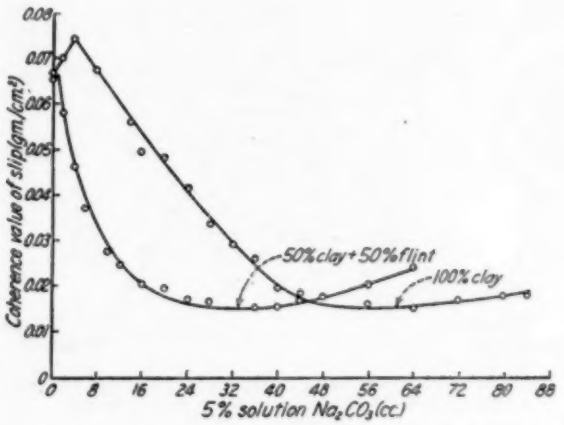

FIG. 33.—Effect of electrolyte (Na_2CO_3) on consistency of Fla. kaolin.

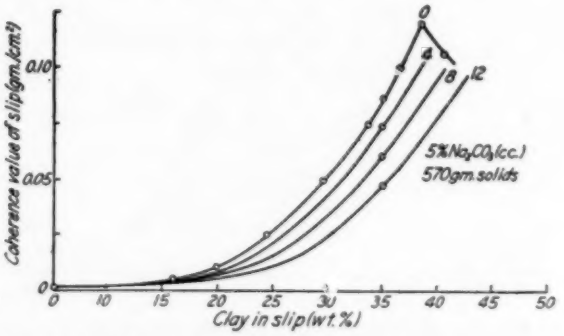

FIG. 34.—Effect of electrolyte additions on consistency of Fla. kaolin.

(3) Aging

The changes in consistency of some clay slips with age are shown in Figs. 31 and 32. Figure 31 shows a plot of coherence value against time of aging for Florida and North Carolina kaolins, both of which are relatively pure clays. A gradual increase of coherence value with time of aging occurs in both cases, which seems to indicate a slaking of the clay as the length of time in contact with water increases. When these data are replotted (see Fig. 32) and the curves are compared with those of Figs. 29 and 30, the effects of aging are seen to resemble those of milling. In many cases, the solubility of some of the batch materials exerts a marked effect on the changes in consistency of slips with time.

(4) Electrolytes

Figure 33 shows the effect of sodium carbonate on a Florida kaolin suspension and also on a mixture of equal parts of Florida kaolin and quartz flint. If similar data are obtained for slips of other concentration, the curve for coherence value versus percentage of solids takes the form shown in Fig. 34.

To understand the fundamental relation in the present phase of the work, a study of the conduct of single-base clays under conditions similar to those described above is desirable. Some clays were prepared for this purpose by a leaching technique, using 0.01 *N* HCl and

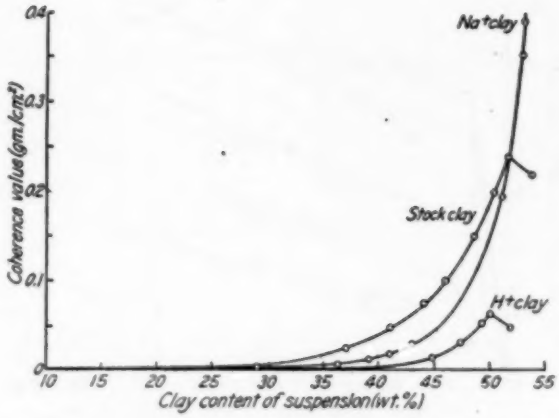

FIG. 35.—Comparison of coherence value-percentage solids curves for Na^+, stock, and H^+ Tenn. ball clay No. 5.

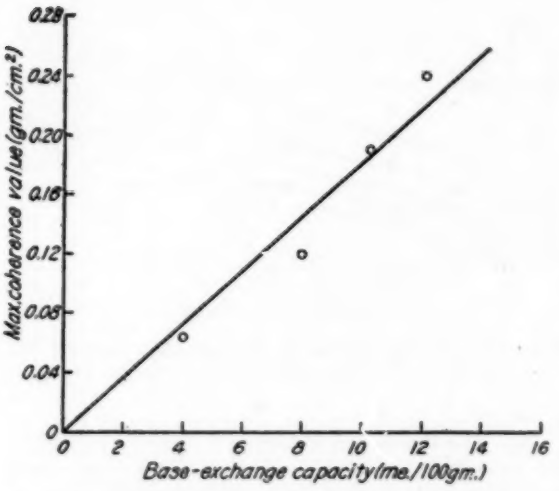

FIG. 36.—Base-exchange capacity versus maximum coherence value of some stock clays.

decanting until no Ca^{++} test was obtained. The clays were then washed with distilled water until the chlorine had been removed.

Tennessee ball clay No. 5 was the principal clay used in this investigation, and the results are shown in Fig. 35. It is well to note the relative heights of the maximum points of the different curves. The sharpness of increase of coherence with concentration is also striking in the sodium clay. According to these results, the hydrogen clay forms what might be termed a "brittle" slip as compared to a "tough" slip with sodium clay.

A significance of the maximum coherence value is demonstrated in Fig. 36, in which the maximum coherence value of various clays is plotted against their respective base-exchange capacities. The correlation is as good as could be expected inasmuch as the tests were made with natural clays and the exchange capacities were determined before milling with no corrections for size reduction during milling.

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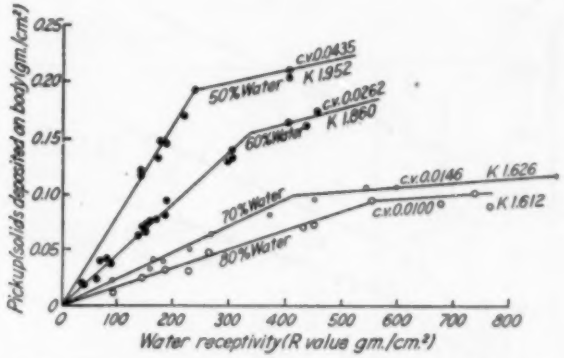

FIG. 37.—R-value pickup curves for slips made of 10% Fla. kaolin, 90% flint; coherence value, c.v.; dry factor, d.f.

(5) Deposition Limit and Deposition Constant

An empirical relationship between coherence value, receptivity, and pickup may be shown by equation (1), see p. 214.

$$P = K\left(\frac{R}{100}\right)(C - 0.001) \qquad (1)$$

The deposition constant defines the relation between receptivity and the coherence value of any given slip or suspension or, expressed differently, the deposition constant may be said to define the rate of deposition of solids from a slip or suspension onto a body.

The equation and consequently the deposition constant does not apply beyond the "deposition limit" without a correction factor. The deposition limit refers to the point at which a break occurs in the R-value versus pickup curve. This break, for the present purpose, is considered to be sharp and is associated with the deposition properties of the slip. This graph may actually be a curved line in the region of the break, but considering it to be the junction of two straight lines does not appreciably alter the ultimate results.

By means of equation (1) and a few simple measurements, it is possible to calculate the deposition constant for a slip or suspension. When the deposition constant has been determined, it may be used to predict other variables in the equation. If the R value of a piece of ware and the desired weight of glaze application are known, it is a matter of simple arithmetic to calculate the proper coherence value at which the slip should be set. This method may also serve as a useful research tool or control test by determining the change produced in the deposition constant by the variables encountered in slip preparation. The same procedure also holds promise as a means of evaluating and controlling certain raw materials.

A few examples of the effect of milling treatment on the deposition constant are given in Table I. The results are shown on the effect of milling a clay and flint mixture with different amounts of water in the same mill for one hour. Some numerical data also illustrate the change in deposition constant of a clay slip milled with varying water additions.

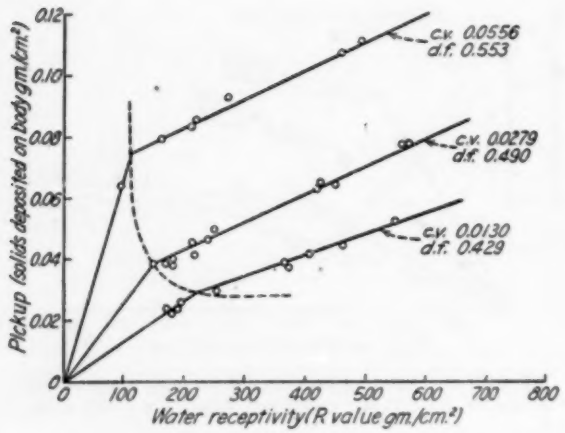

FIG. 38.—R-value pickup curves for slips made of 25% Fla. kaolin, 75% flint; coherence value, c.v.; dry factor, d.f.

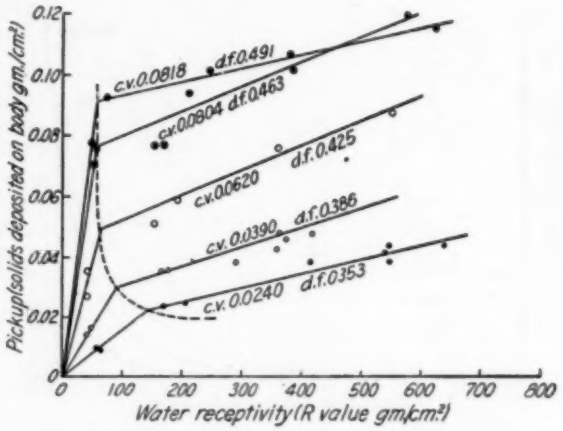

FIG. 39.—R-value pickup curves for slips made of 55% Fla. kaolin, 45% flint; coherence value, c.v.; dry factor, d.f.

TABLE I

EFFECT OF MILLING TREATMENT ON DEPOSITION CONSTANT

Batch No.	Coherence value	Dry factor	Specific gravity	Deposition constant
Clay-flint mixture milled with varying water additions				
1	0.0435	0.6650	1.707	1.952
2	.0262	.6139	1.619	1.860
3	.0146	.5849	1.549	1.626
4	.0103	.5490	1.505	1.617
Clay milled with varying water additions				
6	0.0680	0.322	1.236	0.8234
7	.0566	.3012	1.218	.5400
8	.0398	.2780	1.207	.5160

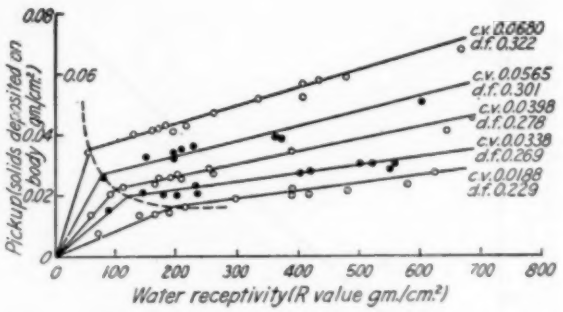

FIG. 40.—R-value pickup curves for slips made of Fla. kaolin; coherence value, c.v., dry factor, d.f.

Sets of R-value versus pickup curves for Florida kaolin and mixtures of Florida kaolin and flint are shown in Figs. 37 to 40. It is characteristic of each of these families of graphs that a hyperbolic curve can be drawn through the breaks (deposition limits), as indicated by the broken lines. There is obviously a relation between coherence value and deposition limit, but the quantitative relation has not been established. Once this relation is established, it is clear that the equation would involve all the quantities, namely, coherence value, pickup, receptivity, deposition constant, and deposition limit. The establishment of such relations remains for future work.

III. Summary

A compilation of the data results in five conclusions.

(1) Equation (1) shows the relation between coherence values, receptivity, and pickup, and it also holds up to the deposition limit.

(2) The maximum coherence value is directly related to the base-exchange capacity and is essentially a straight-line relation in the range studied.

(3) The deposition constant is inversely related to the coherence-value maximum and consequently to the base-exchange capacity.

(4) The deposition constant is directly related to the deposition limit and the slope of the R-value versus pickup curve beyond the deposition limit.

(5) The position of the hyperbolic curve joining the deposition limit points is inversely related to the coherence-value maxima; the higher this maximum, the nearer the hyperbola will be to the axis.

The coherence values are the chief measurements of this system of control and may be used to check incoming raw material as to uniformity and utility. This measurement may also serve as a control test at any point in the process, and by associating the values with other previously mentioned quantities, a remedy will be evident if the slip does not have the proper consistency.

Receptivity is easily measured; the value may be used to good advantage to check the constancy of the processing of the ware and will provide a useful check of the suitability of the ware for glaze application.

Acknowledgment

The authors wish to express their indebtedness and sincere appreciation to C. W. Parmelee for his part in the direction of this project and for his helpful suggestions throughout the investigation.

DEPARTMENT OF CERAMIC ENGINEERING
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

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